MURI: Surface-Templated Bio-Inspired Synthesis and Fabrication of Functional Materials

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14. ABSTRACT

The use of biosynthons and bio-inspired assembly is a new, but extremely powerful approach to the synthesis of designer materials. The development of new methods for patterning biological molecules on the nanometer to micron length scale will lead to new biomaterials that can be used for fabricating a variety of nanostructured organic and inorganic materials that are of vital importance to the Department of Defense. These include catalytic peptide tubes, host-guest materials for molecular separations, quantum dot and magnetic particle arrays, bio-nanocircuitry, photonic bandgap and 3-D power structures, and novel bio-warfare detection materials. This grant has pursued an integrated research effort that has focused on 3 thematic areas of research: A) biocompatible nanolithography methods for patterning and templating of 2-D and 3-D nanostructured materials; B) nucleic acid-based approaches to preparing extended functional architectures both in solution and from predesigned, nanostructured surface templates, and C) protein-based or inspired architectures. The highlights of our accomplishments are featured in the following report.

15. SUBJECT TERMS
bio-inspired assembly, designer materials, Dip-Pen Nanolithography, patterning of biological molecules

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Summary

This final report summarizes major scientific and technological accomplishments during the five years of the MURI grant. It includes an extensive list of over 100 articles published in peer reviewed journals and participation in scientific meetings, workshops, and lectures. Finally, invention disclosures, transitions, and awards earned by the participating investigators are listed. The MURI program was exceptionally productive as can be deduced from the highlights of the scientific and technological breakthroughs in the following paragraphs.

The focus of our effort was in four major areas:

A - Supramolecular assembly using bio-inspired approaches

B - Dip-Pen Nanolithography and its applications

C - Functional materials for data storage, sensing, and diagnostics

D - Development of models and computational tools for self-assembly

In the DPN area, whittling or electrochemical desorption was developed to reduce the size of DPN-generated nanostructures on gold surfaces, and enzymatic polymerization was used in conjunction with DPN patterning of reactive monomers of 4 aminothiophenol and caffeic acid to synthesize conducting polymers. Our MURI-team was also successful in developing new protocols for the assembly of nanoarrays composed of functional antibodies for the detection of the HIV-1 p24 protein.

A novel, high-throughput, high-resolution technique called "On-Wire Lithography" (OWL) was developed for the lithographic processing of one-dimensional metallic nanowires. This technique allowed the routine fabrication of gap structures in the five to several hundred nanometer range. These structures are ideal candidates for nanoelectronic and molecular electronic devices.

The MURI team was particularly successful in developing procedures and protocols for the assembly of organic and inorganic supramolecular architectures covering a wide range of building blocks like cyclic D,L-α- and collagen-like peptides, peptide and DNA-polymer amphiphiles, antibodies, viruses, and composite nanorods.

Lastly, significant progress was made towards understanding, on a theoretical and experimental level, how two model molecules, alkyl thiols and peptide amphiphiles (PA), self-assemble on surfaces. The impact of environmental factors on the shape and properties of these structures was analyzed.

While the majority of our objectives was reached, as well as exceeded, future challenges remain. With regard to other accomplishments, many postdoctoral associates and graduate students were trained in areas of vital importance to the mission of the DOD, with potential payoff for the agency in the future, and the long-term deployment of many applications.

The highlights of our accomplishments are featured in the following report.

1. Status of Work:

The objectives of this project were: 1) to establish the basic chemical and physical rules that govern the use of bio-molecules such as DNA, RNA, PNA, peptides, and proteins for the assembly of two- and three-dimensional organic and inorganic architectures with predictable and useful properties; 2) to merge three-dimensional solution phase nanostructure assembly strategies with surface-directed ones that rely on Dip-Pen Nanolithography (DPN); and 3) to develop computational tools for predicting the structural, optical, electrical, and mechanical properties of these novel templated structures. During the five and a half years significant progress has been made towards all five objectives:

2. Accomplishments/New Findings

A. Supramolecular Assembly Using Bio-inspired Approaches (Ghadiri, Kaplan, Stupp, Mirkin)

A.1. Self-Assembly of Peptide Nanotubes (Ghadiri)

The **Ghadiri** group has focused on exploiting the structural features of self-assembling cyclic *D, L*-α-peptide nanotubes in the context of self-organizing organic conductors and semiconductors. A second objective was to rationally design self-assembling peptide nanotubes carrying different structural and functional features suitable for the fabrication of new biologically active materials.

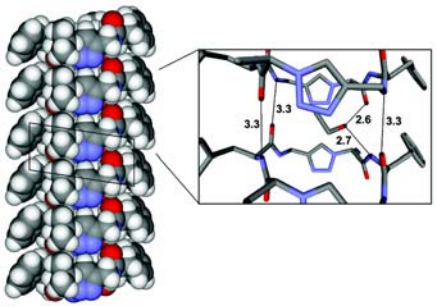


Figure 1. Crystal structure of a self-assembled heterocyclic peptide nanotube featuring novel triazole backbone modifications.

Self-assembled peptide nanotubes have been used as surface templates for the formation of nanocomposites featuring copper and iron-oxides. Appropriately designed cyclic *D, L*-α-peptides can assume flat ring-shaped geometry and stack via directed backbone-backbone intermolecular β-sheet-like hydrogen bonding into open-ended hollow peptide nanotubes. This class of supramolecular assemblies made it possible to use large numbers of side chain variations to equip the nanotube scaffold with different materials and functional characteristics. The identity of the side chain and the placement of the amino acids in the cyclic peptide subunit determine which functional groups will be presented on the surface of the peptide nanotube microcrystals. These highly ordered surfaces with predetermined functional groups were then used to template the growth of inorganic nanocrystals (iron-oxide) and quantum dots (copper oxides).

Cyclic *D, L*-α-peptides have also been patterned on solid surfaces using DPN. These experiments showed that depending on the position of the sulfhydryl group, the presentation of the amino acid side chain functional group could be rigorously controlled, thus yielding peptide nanotube-patterned surfaces of predetermined functional group orientation.

Two distinct approaches have been used to design conductor and semiconductor self-assembled peptide nanotubes. In the first approach, the role of heterocyclic peptide backbone replacements on a nanotube's band structure and density of states (DOS) was investigated assuming that the incorporation of triazole backbone modifications might

allow us to produce low band gap semiconductor nanotubes (Figure 1). An alternative approach exploited inter-subunit side chain-side chain interactions that resulted from the predictable 3-D organization and juxtaposition of amino acid side chains in the peptide nanotube structure.

Several cyclic *D,L*-α-peptides have been synthesized with incorporated naphtyldiimide (NDI) side chain functionality (Figure 2). Initial studies have shown that these peptides produced intense charge transfer (CT) bands upon peptide nanotube self-assembly, and that complementary inter-subunit charge-charge interactions can affect the formation of long-range ordered peptide nanotubes utilizing two different cyclic peptide sequences.

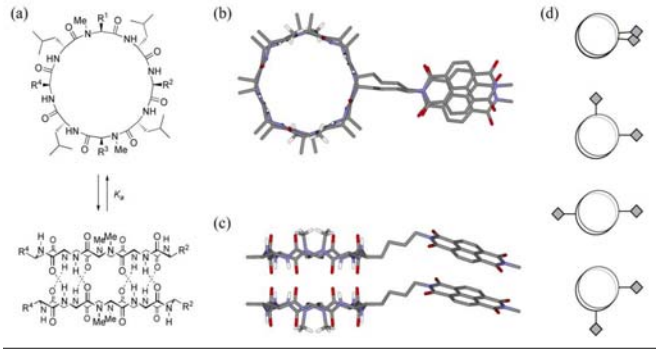


Figure 2. (A) Schematic of hydrogen bond mediated dimerization of *N*-methylated cyclic D,L-α peptides with generic side chains R^1-R^4. **(B)** Model of K-Me dimer viewed from the top, and **(C)** from the side (side chains and protons omitted for clarity). **(D)** Schematic of the overlap of NDI side chains (diamonds) in the four possible dimeric ensembles available to C_1 symmetric peptides K-*i*Bu, O-*i*Bu, and K-Me.

An alternative approach leading to conducting nanotubes, which was based on a strategy termed "supramolecular design by covalent capture" was also pursued. This approach used eight-residue cyclic *D,L*-α-peptides bearing thiophene or dieyne side chains, which can self-assemble via directed hydrogen bonding interactions into the thermodynamically favored β-sheet-like tubular structures. In these nanostructures the thiophene or dieyne side chains were located on opposite ring stacks in close van der Waals contact. Subsequent initiation of thiophene or dieyne polymerization produced a covalently captured nanotube with polythiophene or polyene nanowires along the length of the cylindrical structure. Recent studies have suggested that cyclic peptides bearing thiophene or dieyne substituents can undergo polymerization under appropriate reaction conditions.

By incorporating appropriate amino acid side chain-side chain stacking interactions capable of ground state and/or excited state charge transfer, desired levels of semiconductor characteristics could be obtained. In particular, a concise and convergent method for the synthesis of cyclic peptides bearing 1, 4, 5, 8-naphthalenetetracarboxylic diimide (NDI) side chains was developed to modify the electronic structure of the peptide through increased interactions between aromatic moieties through peptide backbone self-assembly.

Structural and photoluminescence studies of these molecules in solution showed that a propensity for self-assembly of the D, L-α-cyclic peptide backbone enhances intermolecular NDI excimer formation. Furthermore, the efficiency of charge transfer in the supramolecular assembly depended on the length of the linker between the NDI and the peptide, the distal NDI substituent, and the number of NDIs on the peptide.

These studies provided insight into the structural requirements for favorable peptide side chain NDI-NDI interactions, and suggested that combining the self-assembly propensity of cyclic D,L α-peptides with NDI derivatives is a promising design approach for novel peptide nanotubes with engineered electronic properties (Figure 3).

A.2. Self-Assembled Peptide Nanotubes with Delocalized Electron Systems (Ghadiri)

The **Ghadiri** lab has designed an eight residue cyclic D,L-α-peptide composed of four cationic 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) side chains (Figure 3), which will in aqueous solution undergo redox-triggered self-assembly into peptide nanotubes with highly delocalized electronic states. Using this approach isolated peptides nanotubes hundreds of nm in length were generated, which subsequently were adsorbed onto solid surfaces (Figure 4).

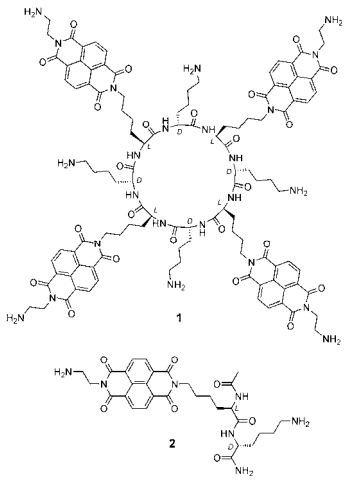


Figure 3. Chemical structure of the NDI-modified peptides.

Self-assembled cyclic D,L-α-peptide nanotubes are electronic insulators. Theoretical studies have demonstrated that a change in the sequence of the cyclic peptide will alter the band gap of peptide nanotubes. Natural amino acid side chains are, however, inadequate to generate electronically conductive assemblies. Since NDI derivatives with extended stacked ring configurations can be used to fabricate organic electronic materials, it was assumed that hydrogen bond directed self-assembly of NDI-bearing cyclic D,L-α-peptides could be used as a tool to generate electronically active ordered biomaterials through promotion of intermolecular stacking of NDI side chains. The feasibility of this basic design concept was confirmed for cylindrical assemblies of dimeric cyclic D,L-α-peptides, and it was shown that intermolecular peptide self-assemblies can serve as effective templates to promote ring stacking and charge transfer between NDI side chains. In summary, **Ghadiri's** research demonstrated that directed backbone hydrogen bonding interactions in self-assembled cyclic D,L-α-peptide nanotubes could promote long range supramolecular orders, and could indeed provide a facile method to prepare a new class of synthetic biomaterials with extended charge delocalized states.

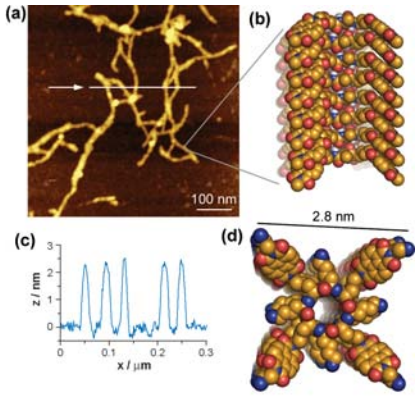


Figure 4. (a) AFM image of reduced cyclic peptide **1 (Figure 3)** adsorbed on mica. (b) Proposed model of the organization of self-assembled cyclic peptides within the fibrous material. (c) The lateral cross-section is consistent with the calculated diameter of the self-assembled peptide nanotube as shown in (d).

A.3. Collagen-like Peptides and their 3-D Structure (Kaplan)

The **Kaplan** lab has used collagen as a model system to study how differences in organic substrate assembly and organization can influence subsequent mineralization patterns.

Collagen constitutes a large family of glycine-rich extra-cellular matrix (ECM) proteins that provide a structural framework for cells and tissues. Native collagen forms triple helical rod-like structures, in which the amino acid glycine is placed at every third position. Substitution of glycine with a different amino acid will disrupt the molecule's ordered structure, and

produce disordered triple helical collagen structures with strong affinity for native and gelatinized type I collagen as templates (Figure 5). This structural change can be propagated up to higher length scales as the molecules assemble further. The influence of altering certain amino acids in collagen-like peptides was investigated with respect to surface patterns, and a series of collagen-like peptides, in which glycine was systematically substituted with bulkier amino acids like alanine, valine or aspartic acid was studied. AFM imaging showed that the change in "packing" was proportional to the size of the substituted amino acid (alanine < valine < aspartic acid), a trend that was reflected in the topography and phase lag images (Figure 6). These experiments demonstrated that the size of the crystals depended largely on the collagen-like peptide sequence used for crystallization, and decreased in the following order: native collagen > alanine mutant > valine mutant > aspartic acid mutant. Similar trends in size reduction were observed with AFM on gold surfaces. Based on these studies it could be concluded that native collagen and the alanine variant display relatively ordered surfaces, while the less ordered valine and aspartic acid variants exhibit clusters. Furthermore, when the peptide variants were used for crystallization larger and thicker crystals could be grown.

Peptides	Sequence
Native	CGKO $(GPO)_2$ GEO $(GPO)_2$ GRO $(GPO)_2$ GDO $(GPO)_5$
OI-A	CGKO $(GPO)_2$ GEO $(GPO)_2$ GRO APO GPO GDO $(GPO)_5$
OI-V	CGKO $(GPO)_2$ GEO $(GPO)_2$ GRO VPO GPO GDO $(GPO)_5$
OI-D	CGKO $(GPO)_2$ GEO $(GPO)_2$ GRO DPO GPO GDO $(GPO)_5$

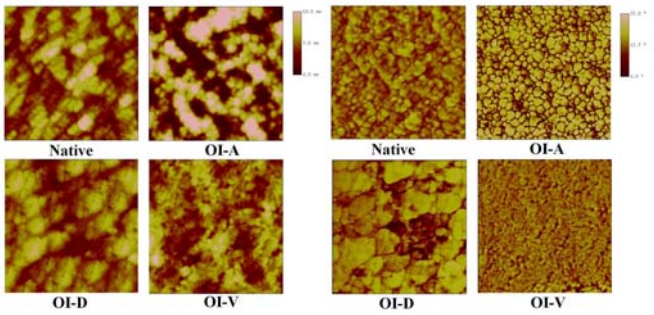


Figure 5. Collagen Peptides and Control of Structural Organization. AFM topography (left) and phase (right) images of collagen peptides drop-cast on gold surfaces (scan size 1 μm^2). Native collagen and the alanine variant displayed relatively ordered surfaces while the valine and aspartic acid variants were less ordered.

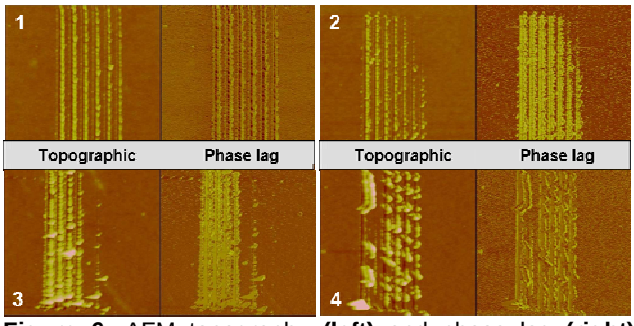


Figure 6. AFM topography **(left)** and phase lag **(right)** images of collagen-like peptides. **(1)** Native with glycine, **(2)** alanine substitution, **(3)** valine substitution, and **(4)** aspartic acid substitution.

A.4. DNA – Polymer Amphiphiles and Micelle Formation (Mirkin)

Amphiphilic block copolymers composed of at least one hydrophobic polymer block and one hydrophilic block have been shown to generate in solution or at biphasic interfaces ordered supramolecular structures such as monolayers, micelles, vesicles, bilayers, helices, and rod- and sheet-like structures. A general solid phase synthesis strategy was designed to synthesize hybrid DNA-hydrophobic polymer amphiphiles (Figure 7).

DNA amphiphiles were prepared via solid-phase synthesis on controlled pore glass beads (CPG) similar to conventional oligonucleotide synthesis. The key reagent required for this synthesis is a polystyrene phosphoramidite (Figure 7-1), which was used to couple the polystyrene fragment to alcohol-terminated oligonucleotides directly off the CPG. The polystyrene-DNA conjugate (Figure 7-2) is soluble and can subsequently be extracted from the CPG with DMF. The molecular weight and structural assignment were confirmed by MALDI-TOF mass spectroscopy, and the purity of the polystyrene-DNA conjugate assessed in a gel electrophoresis migration-shift assay.

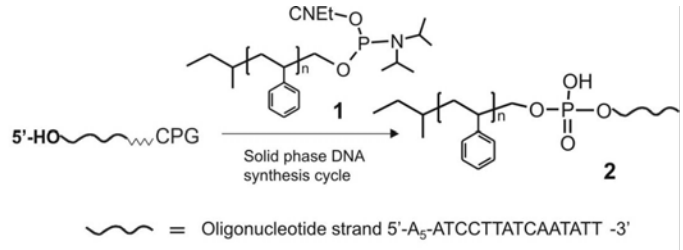


Figure 7. Synthetic route to polystyrene-DNA amphiphilies.

The amphiphilic polystyrene-DNA conjugate formed stable suspensions in various solvents including CH_2Cl_2, THF, DMF, and H_2O. To take advantage of the recognition properties provided by the DNA part, studies were initially performed in water, and the micelles formed in aqueous solutions imaged by TM-AFM, which revealed a dense layer of spherical particles with diameters in the 13 to 18 nm range. The size distribution of the DNA-polystyrene micelles was measured in solution by dynamic light scattering, and found to be consistent with an average particle diameter of 16.4 nm. This suggested that the cores of the micelle assemblies were nearly solid, and that almost all of the DMF was removed after dialysis. Similarly, a series of polystyrene-DNA amphiphiles of different oligonucleotide length (5mer, 10mer, and 25mer) and polystyrene molecular weight (4.1K, 7.2K, and 9.5K) were synthesized that gave micelle structures with average diameters in the 8 to 30 nm range. Since the micelles exhibited unique sequence-specific recognition properties that were derived from the hydrophilic DNA shells, they could be utilized for the rational assembly of nanostructures through DNA hybridization.

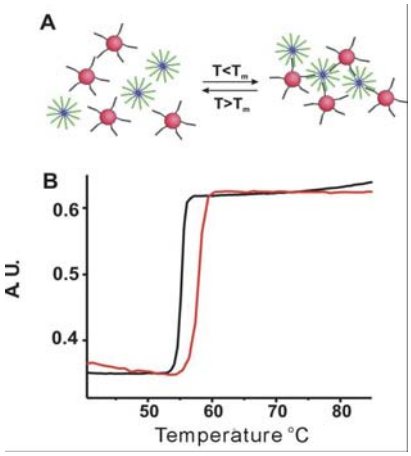


Figure 8. (A) Sequence specific assembly of DNA-polymer micelles and DNA modified gold nanoparticles. **(B)** Melting transitions at 520 nm vs. solution temperature. **Red Curve:** assemblies formed from DNA micelles and gold nanoparticles modified with complementary oligonucleotides. **Black Curve:** assemblies formed from DNA micelles and gold nanoparticles modified with single base mismatch oligonucleotide strands.

DNA-modified gold nanoparticles have been widely used as inorganic building blocks for the construction of many new types of superstructures. The **Mirkin** group has explored the use of these micelle structures as novel organic building blocks in analogous schemes. For example, when solutions of DNA micelles and 13 nm Au nanoparticles modified with complementary oligonucleotides (5'-SH-A5-AATATTGATAAGGAT-3') were mixed sequence specific assembly took place. This process was reversibly, and heating of the reaction above the melting temperature (T_m = 57.8 ºC) of the duplex strand separated

the duplex strand into two single strands. The sequence-dependent nature of the assembly could be illustrated when oligonucleotide strands with a single base mismatch were used. The melting temperature of aggregates formed from micelles and 13 nm Au nanoparticles modified with oligonucleotide strands carrying a single base mismatch was found to be 2.6 degrees lower (55.2 ºC) than for the aggregates formed from perfectly complementary strands (Figure 8). The reason of the sharp melting transitions (FWHM = 2-3 ºC) is well understood and could be explained by a cooperative melting model developed by the **Schatz** group for analogous gold nanoparticle and comb polymer systems.

A.5. Metal-Organic Based Biomolecule Nanoarrays (Mirkin)

DPN has facilitated the massive miniaturization of microarray technology and provided the tools to address questions that could not be addressed with microarrays or bulk systems including the formation of larger, denser libraries for screening of chemical and biological systems, and the study of interactions between complex biological entities such as viruses, cells or proteins.

A.5.1. Single Virus Nanoarrays

DPN has achieved a level of resolution and sub-100 nm miniaturization that has made it possible to undertake such projects like isolating nano- and microscale biological entities at the single-particle level *in situ*, and controlling the orientation of individual entities at the molecular level.

The **Mirkin** lab has developed a novel strategy that uses a combination of DPN and complex coordination chemistry to immobilize and position individual virus particles on surfaces. As a model system to confirm the feasibility of this approach Tobacco Mosaic Virus (TMV), an anisotropic tubular structure 300 nm long and 18 nm wide, with a well-characterized carboxylate-rich surface, was chosen.

Typically MHA features were generated by DPN on a gold substrate, and MHA-free areas subsequently passivated with 11-mercaptoundecyl-tri(ethylene glycol) (PEG-SH) to minimize non-specific binding. After incubation with $Zn(NO_3)_2$ the nanoarrays were immersed in a solution of TMV to allow assembly of viral particles on the nanoarrays. The presence of viral particles assemblies on the templated nanoarrays was confirmed with an anti-TMV antibody. Based on these experiments it was concluded that 350 nm x 110 nm MHA features spaced one micrometer apart were ideal to assemble individual particles. Indeed, when 350 nm x 110 nm MHA features perpendicular to one another were used for viral particle assembly, an array of site-isolated single TMV particles perpendicular to each other was obtained (Figure 9). A comparison of AFM images of viral arrays before and after treatment with anti-TMV antibodies showed a height increase of approximately 9 nm, which is consistent with the height of the antibody.

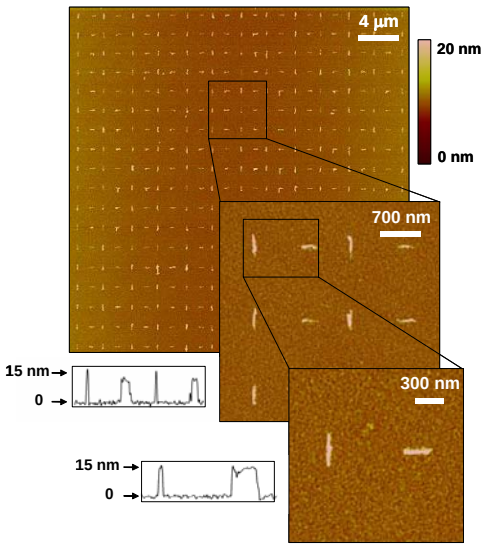


Figure 9. AFM images and height profiles of a perpendicular single TMV nanoarray.

A.5.2. Functional Antibody Nanoarrays (Mirkin)

One of the key challenges in the fabrication of functional micro- and nanoarrays for high-throughput bio-detection applications is the immobilization of antibodies in such a manner that recognition sites are left intact and accessible to antigens. The **Mirkin** group has solved this problem by developing a metal-organic protocol that allows one to control the orientation of antibodies on surfaces in such a way that the antigen-binding regions (F_{ab}) are exposed. Previous antibody immobilization techniques either relied on binding proteins like protein A, G, A/G and L, or fusion proteins/antibodies with unusual binding tags for surface attachment, electrostatic or covalent linkage or a combination of both.

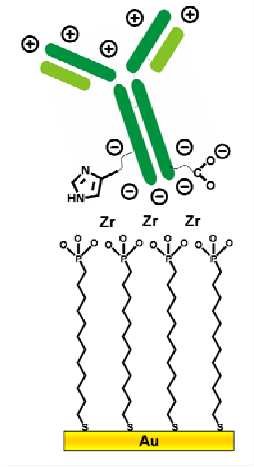


Figure 10. Antibody immobilization on a $ZrOCl_2$ treated TDP monolayer.

Our innovative technique exploited differences in the isoelectric points (pI) of the F_{ab} and F_c antibody fragments for surface-binding of metal-ions, which in turn will bind antibodies in such a way that the F_{ab} fragments are pointing away from the surface (Figure 10). Since the pI of the F_{ab} region is generally higher and the pI of the F_c region lower than the pI of the entire antibody, the F_c and F_{ab} regions are negatively and positively charged. Thus, by working at a pH near the pI, functional groups such as the imidazole or carboxylate groups of the negatively charged F_c regions will preferentially bind metal ions like Zr(IV) or Zr(II) (Figure 10).

Using the aforementioned approach DPN was used to generate 12-mercaptododecayl-phosphonic acid (MDP) and MHA features. The exposed functional groups of the MDP and MHA features were subsequently coordinated using Zr(IV) and Zn(II) metal ions, unpatterned areas passivated with PEG-SH, and the metallated arrays exposed to antibody. Oriented unmodified poly- and monoclonal antibodies nanoarrays were generated (Figure 11) by assembling goat IgG, mouse IgG1, chicken IgY, rabbit IgG and mouse IgM antibodies on the nanoscale features of the metal coordination complexes. The respective height increases for the assembled coordinated complexes were 6.5 ± 1.0 nm, 5.3 ± 0.7 nm, 3.9 ± 0.6 nm, 8.0 ± 1.2 nm and 2.8 ± 0.5 nm, respectively.

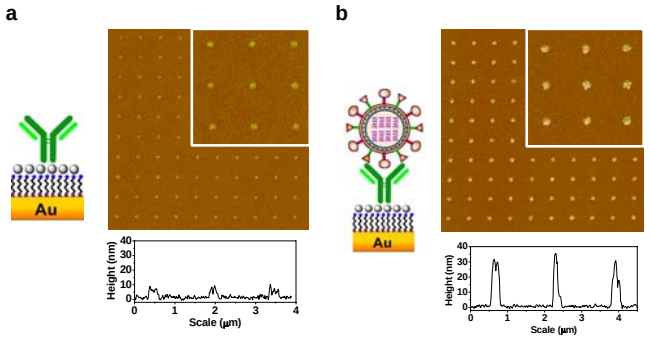


Figure 11. TM-AFM images of nanoarrays of SV5 virus specific rabbit IgG. **a.** Topography image and height profiles of rabbit IgG on an array of 550 nm MHA dot features pretreated with $Zn(NO_3)_2{\cdot}6H_2O$. **b.** Binding of Influenza A virus to the array in a. AFM images were taken at the same location (with zoomed in inserts) with a scan rate of 0.5 Hz. Scale bars are mm for the large arrays and 500 nm for the insets.

The biological activity of the surface-immobilized antibodies was probed by incubation of the arrays with the corresponding antigens, which were the 12CA5 epitope of the influenza A hemagglutinin for the goat IgG, mouse IgG1 and chicken IgY antibodies, simian virus 5 (SV5) for rabbit IgY, and the estrogen

receptor β (ER-β) for mouse IgM. Height increases of 23 ± 2 nm, 29 ± 1 nm and 24 ± 2 nm confirmed that goat IgG, mouse IgG1 and chicken IgY recognized the Influenza A virus particles. Binding of immobilized rabbit IgY and mouse IgM to SV5 particles and the estrogen receptor β, respectively, was confirmed by a height increase of 25 ± 2 nm.

Antibody nanoarrays were also generated by multi-pen DPN. In a proof-of-concept experiments influenza virus particles were directly captured on mouse IgG1 anti-HA parallel nanoarrays, the immobilized viruses complexed with an anti-HA antibody, and immobilized in a sandwich complex. Particles bound to influenza virus were subsequently treated with a secondary goat anti-mouse antibody labeled with fluorescent Alexa Fluor 488. The assembled complex was detected by TM-AFM, and showed a height increase of 45 ± 3 nm, the expected height for the sandwich complex.

To conclude, this technique can potentially detect clinically relevant antigens in nano- to picoliter volumes with detection limits surpassing those of the conventional ELISA based immunoassays. It is anticipated that this technique will have significant impact on a range of applications such as proteomic analysis, and 2-D or 3-D crystalline arrays for protein structure analysis.

A.6. Self-Assembly of Peptide Amphiphile Nanofibers (Stupp)

Work in the **Stupp** lab has centered on the synthesis of new PA-derived self-assembly systems, and on the manipulation of the respective supramolecular nanostructures. Several strategies were applied to exert a high degree of position and orientation control over these nanostructures

A set of peptide amphiphiles that self-assemble at low pH into high aspect ratio nanofibers has been designed (Figure 12). Modification of the peptide sequence in the amphiphilic molecule led to different types of molecular recognition sites on the fibers' surfaces, which also allowed nucleation of different inorganic materials. Furthermore, these peptide-based systems can self-assemble at neutral pH in the presence of divalent and trivalent metal ions like copper, barium, zinc, cadmium, and iron, which is important since the same ions that promote self-assembly can also serve as precursor ions for nucleation of inorganic crystals on the nanofibers. Highly charged examples of these peptide amphiphiles were designed to promote on metal oxide surfaces self-assembly into very large arrays of parallel nanofibers. Organized self-assembly of these nanostructures was achieved by evaporation of water from dilute solutions of the peptide amphiphiles. The peptide sequence of these molecules contained phosphoserine, aspartic acid, and cysteine residues for crosslinking of the supramolecular structures.

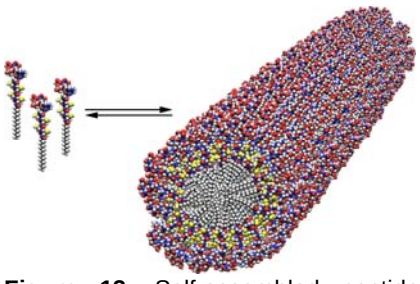


Figure 12. Self-assembled peptide amphiphile nanofiber.

The first surface tested was titanium dioxide, and it could be shown that aminosilane treatment of these surfaces stabilizes the nanofibers when exposed to an aqueous medium. Parallel arrays of these nanofibers can have dimensions on the order of one micron or more. Combined with patterning techniques these systems produced highly functional 2-D structures that utilize self-assembly as the initial step.

A.7. Alignment of PA-based Supramolecular Structures (Stupp, Mirkin)

Several strategies were developed to exert a high degree of orientation control over PA supramolecular nanostructures. These surface-confined nanostructures were then used for bio-inspired interactions and to template the mineralization of inorganic materials.

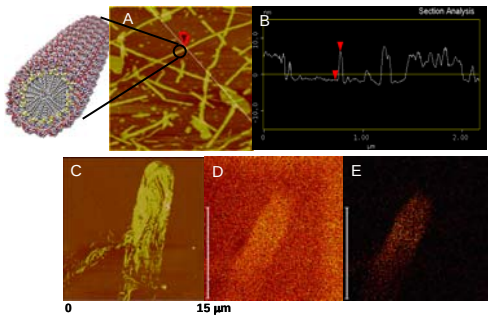


Figure 13. AFM topography images (tapping mode) of PA fibers formed on silicon from a DPN ink (3.5 % glycerin in water). **(A)** Random PA network, and **(B)** the associated height profile. **(C)** Dense PA feature (image length = 15 mm) used for SIMS, with **(D)** hydroxide ions and **(E)** cyanide ions.

Previously, micro-contact printing (µ-CP) on gold was used to construct well-defined surface patterns from bioactive PAs. PA solutions were used as DPN inks that formed organized nanofibers upon evaporation of the ink. Nanofibers produced using this technique were comparable to those predicted by molecular modeling, and were corroborated by TEM data (Figure 13 A, B). Furthermore, secondary ion mass spectroscopy (SIMS) indicated that the PA fiber layer generated a high density of cyanide ions, which is indicative of the presence of amide bonds in the PA molecule as opposed to background hydroxides. Through optimization of the writing speed and ink composition it was possible to direct the length of the fibers. For example, shorter fibers were observed at slower writing speeds, while longer fibers were produced at faster writing speeds. Furthermore, silane tip modifications ultimately made it possible to generate patterns with several domains of aligned PA fibers.

In a parallel approach diaminopyridine alkanethiol (DAP) was used as a generic DPN ink capable of interacting with different PAs. Additionally, the PA paradigm was extended to include nucleosides (e.g. thymine). Exposure of a DAP patterned surface to the thymine-PA hybrid promoted *in situ* patterning of PA mediated by the DAP surface (Figure 14).

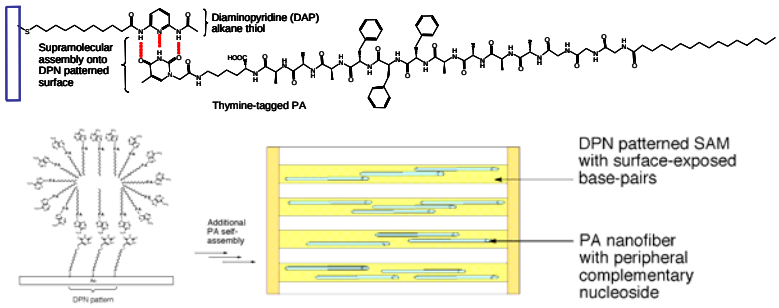


Figure 14. Supramolecular PA patterning mediated by DAP-thymine hydrogen bonding. The DAP pattern was formed with DPN, followed by exposure to thymine-PA.

SEM images of PA dip-coating of polyethylene glycol (PEG)-silane and amino-silane modified silicon nitride AFM tips revealed that PEG greatly suppressed nanofiber formation, which explained the close-packed nanofiber pattern. Presumably these close-packed nanofiber structures originated from self-assembly mediated by the silicon substrate. Direct patterning on different surfaces, like freshly-cleaved mica, hydrophilic silicon and hydrophobically modified substrates revealed that hydrophobic surfaces maximized pattern resolution. In addition to direct patterning an indirect approach was also explored.

A preferential desorption method was developed. An excess of PA was deposited onto a patterned self-assembled monolayer (SAM), followed by treatment with KOH solution to preferentially desorb the nanofibers from MHA. AFM and Secondary Ion Mass Spectrometry (SIMS) revealed that the surface was covered with monolayers of PA nanofibers, only the MHA patterns were excluded (Figure 15). The PA nanofiber patterns replicated the alkyl-thiol DPN pattern reproducibly. Shorter exposure to KOH led to under-developed patterns with some nanofibers bridging the MHA area (Figure 15), which demonstrated that this was indeed desorption rather than adsorption.

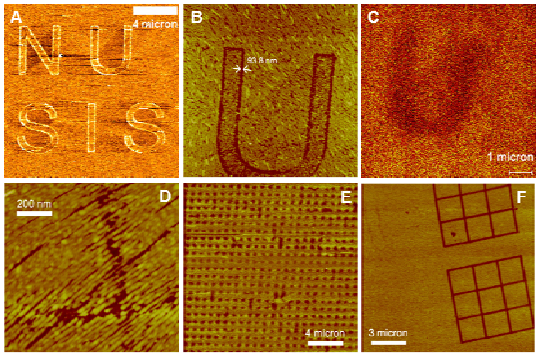


Figure 15. (A) Lateral force microscopy (LFM) of MHA DPN pattern on gold. **(B)** TM-AFM topography of the letter U after desorption. **(C)** SIMS mapping of cyanide ions of the same area as (B). **(D)** TM-AFM of nanofiber pattern. **(E)** LFM of MHA micro-contact printed lines. **(F)** LFM of ODT DPN pattern on MHA background.

In order to induce alignment of the self-assembled PA nanofibers on surfaces, a controlled evaporation method utilizing the shear effect of a receding solution edge during evaporation was developed (Figure 16). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) revealed the microscale morphology of the aligned arrays of PA nanofibers. The β-sheet structural model and polarization-modulation infrared spectroscopy in transmission mode revealed the in-plane orientation of monolayer-thick nanofibers over macroscopic areas.

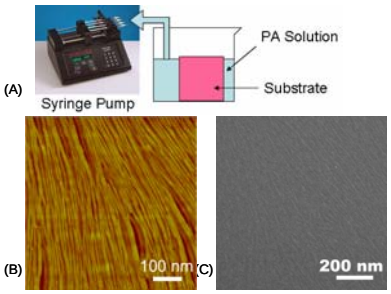


Figure 16. **(A)** Schematic of the controlled-evaporation alignment setup. **(B)** TM-AFM and **(C)** SEM images of PA an aligned nanofiber array.

A.8. Peptide-Lipid (PL) Based Self-Assembly (Stupp)

Another self-assembly system based on peptide-lipid (PL) hybrid molecules and similar to the PA model was developed. PL molecules can self-assemble in non-polar organic solvents into one-dimensional nanofibers with binding functionalities (Figure 17). An expansion of this system to non-aqueous environments will make it possible to use PLs for the formation of ordered patterns in a much wider range of functional materials. As a first step in this direction one-dimensional arrays of lipophilic nanocrystals were synthesized through modification of the nanocrystal surface with functional groups complementary to those on the nanofibers.

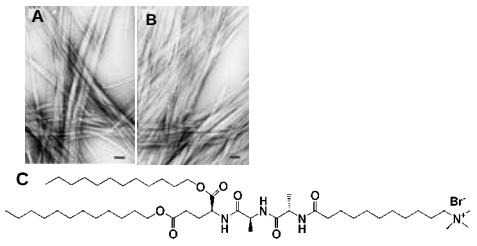


Figure 17. **(A, B)** TEM of 1-D PL-based organic nanostructures in an apolar organic solvent. **(C)** Molecular structure of PL

Two key contributions, the synthesis of molecular scaffolds with self-assembling properties and the control of bio-inspired

surface assemblies, are essential for the development of new hybrid materials with applications in bio-sensing, biological signal transduction and crystallography-controlled mineralization. A full understanding of such self-assembled nanostructures and how to control the position and orientation of structures carrying peptides or other biological relevant epitopes will be of significant scientific importance, and will most likely also yield novel materials composed of functional hybrid nanostructures.

A.9. Composite Nanorods and their Assembly into Three-dimensional Superstructures (Mirkin)

Two-domain segmented metal-polymer nanorods were prepared using electrodeposition of gold into porous aluminum templates, followed by electrochemical polymerization of pyrrole, and assembly of the nanorods into uniform bundles. Packing theories predict that the driving forces for the assembly are strong π-π stacking interactions among the polymer rods, which are induced by the highly ordered chains along the polymer fiber walls. Assembly into uniform bundles is further facilitated by van der Waals interactions between the gold segments of the nanostructures. The curved shapes are believed to be due to the strong hydrophobic interaction between the polymer domains, and the volume difference between gold and polymer domains (Figure 18). Careful control of the polymer/gold ratio during synthesis allowed one to produce 3-D tubular shapes composed of gold-polymer wires (Figure 18). This synthesis represents a new approach to produce mesoscopic structures since the structural shape of the final, assembled structures could be controlled by the metal-polymer component ratios in the individual nanorods.

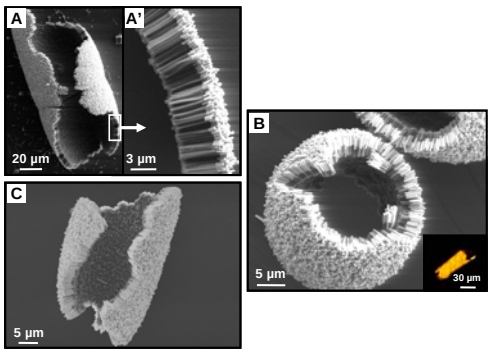


Figure 18. SEM images of 3-D superstructures of Au-polymer composite nanorods. Au/polymer length ratio. **(A)** ~ 2/8, **(B)** ~ 6/4, and **(C)** ~ 8/2.

B. Dip-Pen Nanolithography and Its Applications (Mirkin, Dravid, Ginger, Kaplan, Ratner, Schatz)

B.1. Strategies to Improve DPN Resolution (Mirkin)

A novel strategy, called whittling or electrochemical desorption, was used to reduce the size of DPN generated alkanethiol nanostructures on gold surfaces. This strategy represents a simple and convenient method to enhance the resolution of DPN, and can potentially also improve the resolution of other soft lithography techniques. By applying a potential of –750mV over a dot array using a conventional three-electrode cell, the size of DPN patterns was reduced from 90 nm to 55 nm. This approach effectively reduced the diameter of these structures at a rate of ~1 molecule/sec. Since the perimeter of these patterns is rich in defect sites, nanostructures could gradually be whittled away at a rate dependent on the time and potential applied. By applying this procedure to structures patterned on atomically flat surfaces, the current 15 nm resolution limit of DPN could be broken.

The whittling process was studied as a function of substrate morphology, adsorbate head and tail groups, electrolyte solvent and salt. An example of the effect of electrochemical whittling on arrays generated by μ-CP is shown in Figure 19. The spots on the MHA array were reduced to 1/10 of the original size, while the spots on the 1-octadecanethiol (ODT) array are only reduced by 1μm. In conclusion, electrochemical whittling made it possible to address nanostructures of different adsorbates independently. The miniaturization of these features was based upon a judicious selection of adsorbate, applied potential, and supporting electrolyte.

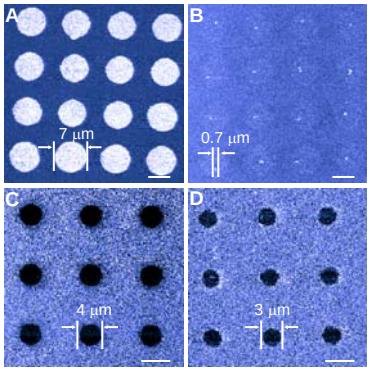


Figure 19. LFM images of μCP-patterns before **(A, C)** and after **(B, D)** electrochemical whittling.

B.2. Synthesis of Conducting Polymers using a DPN-Biocatalytic Approach (Kaplan)

Enzymatic polymerization in conjunction with DPN patterning of reactive monomers was used to form conducting polymers under ambient conditions. Enzymatic polymerization methods offer several advantages, which are: (a) labile biological molecules can be used, (b) interfacing with cells, enzymes and other bio-recognition elements through "nanoscale wiring" is possible, and (c) control over the surface orientation of the monomers and the resulting polymers can be achieved. In the present study DPN was extended to enzymatic processes for surface-patterning of conducting polymers. The Kaplan group has studied three systems: Caffeic acid, 4-aminothiophenol, and two tyrosine derivatives.

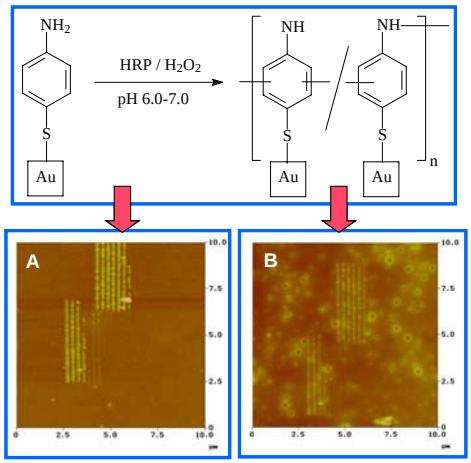


Figure 20. Enzymatic Polymerization of 4-aminothiophenol using DPN. DPN features are: **(A)** 150 nm wide, 25 nm high, and **(B)** 200 nm wide, 15 nm high.

B.2.1. 4-Aminothiophenol

The usual methods for the synthesis of poly-aniline and its derivatives are either electrochemical or chemical. Horseradish peroxidase catalysis represents a novel approach, and was successfully used for the polymerization of 4-aminophenol, and the formation of conjugated polymeric backbones under ambient conditions (Figure 20).

The polymer could be removed from the gold surface, and analyzed by mass spectrometry, which indicated molecular weights of up to 1000 Da. 4-Aminothiophenol patterns before and after HRP catalyzed polymerization were characterized by electrostatic force microscopy (EFM) with conducting polyaniline and sulfonated polystyrene (SPS) as controls. Compared to the non-conducting and conducting polymer controls, the phase shift decreased after enzymatic polymerization, which indicated a conductive polymer backbone.

B.2.2. Caffeic Acid

Caffeic acid (3,4-dihydroxy-cinnamic acid) is a naturally occurring lipoxygenase inhibitor and radical scavenger that is usually found in conjugated forms like chlorogenic acid. The caffeic acid monomer was polymerized on three different surfaces using DPN, and the orientation of the polymer on the surface investigated (Figure 21). Patterning conditions were optimized with methanol/H_2O_2. Caffeic acid patterns were only obtained on 4-aminothiophenol modified gold surfaces. EFM images indicated that the length of the polymer increased with enzymatic polymerization. X-ray Photoelectron Spectroscopy (XPS) demonstrated polymerization of monomeric caffeic acid and revealed primarily C-C coupling. The two hydroxyl groups on the benzene ring, which form quinone structures during *in situ* surface polymerization, were not involved in the formation of the polymer backbone. Importantly, polymerization of caffeic acid in solution produced mixed products with C-C and C-O-C coupling, while *in situ* polymerization on surfaces produced no C-O-C coupling. This difference was most likely due to surface induced orientation facilitated by the DPN process. Thus *in situ* surface polymerization led to a structure different from the one that could be obtained through bulk reactions.

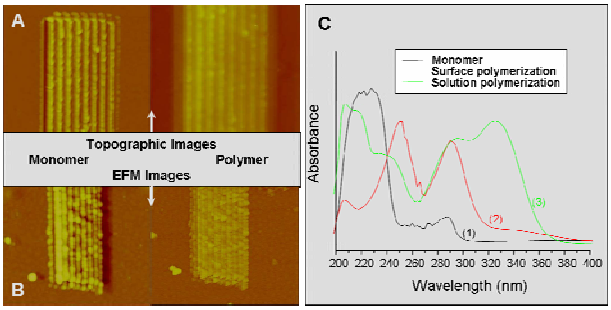


Figure 21. **(A)** Topographic images of caffeic-acid patterns on 4-aminothiolphenol modified gold before **(left)** and after **(right)** enzymatic polymerization. **(B)** EFM images of the (left) monomer and (right) polymer patterns on ATP modified gold surface. **(C)** UV-Vis spectra of the caffeic-acid monomer (grey), polymer after removal from the surface (red), and polymer prepared in solution (green).

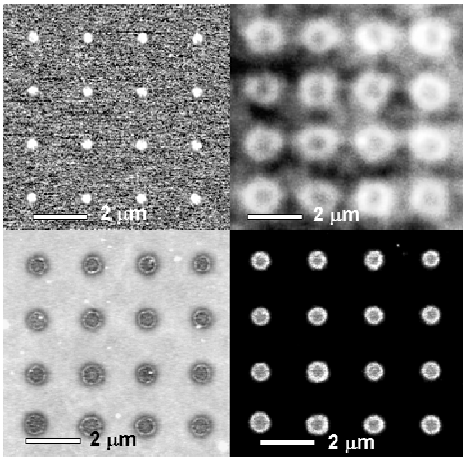


Figure 22. **(A)** LFM image of DPN-MHA template on benzenethiol background. Micrographs show the same substrate region after spin-coating a 35 nm-thick film of a 60:40 blend of polystyrene/polythiophene from a chlorobenzene solution. **(B)** Fluorescence image. **(C)** AFM topography. **(D)** Conducting AFM image.

B.3. Formation of Thin Films Using DPN (Ginger)

Phase separation and de-wetting in thin polymer films are problems of long-standing technological importance, and are directly relevant for the performance of thin-film optoelectronic devices fabricated from blends of semi-conducting conjugated polymers. Because the characteristic length scales associated with the electronic excitations in conjugated polymers are on the order of a few to a tens of nanometers, the control of phase separation in conjugated polymer blends on these same length scales represents a significant challenge.

DPN was applied to the problem of morphological control in spin-coated films of conjugated polymers. It was demonstrated that nanoscale DPN templates could be used to guide and direct nucleation, growth, and

pattern formation of various polymer phases during spinodal decomposition. The resulting films were characterized by a combination of optical and scanning probe microscopy, and spectroscopy (Figure 22). In conclusion, DPN is a useful tool for studying and controlling template directed phase separation in thin films of conjugated polymers. This research will be of direct technological relevance for optimizing the performance of thin-film photonic and optoelectronic devices including light-weight, low-power, flexible light-emitting diodes and solar cells for applications relevant to the DoD.

B.4. Peptide and Protein Nanoarrays for the Detection of HIV-1 p24 (Mirkin)

A protocol was developed to use Direct-Write DPN to generate multi-component, biologically functional protein nanoarrays on Au and Ni oxide surfaces. Using this protocol, a functionally active immunoglobulin-gamma (IgG) protein nanoarray with feature sizes of 40 nm was generated. The bio-recognition properties of the IgG protein nanoarray were confirmed by incubation with Au nanoparticles coated with anti-IgG. Using a similar approach, histidine (His)-tagged ubiquitin and thioredoxin protein nanoarrays were generated by direct-write DPN on Nickel (Ni). The biological activity of ubiquitin protein nanoarrays was verified by fluorescence microscopy after incubation of the nanoarray with fluorophore-labeled anti-ubiquitin.

Using the above approach the **Mirkin** group developed an assay for the detection of the HIV-1 p24 protein in plasma samples using DPN-fabricated nanoarrays of anti-p24 monoclonal antibodies. Gold nanoparticles modified with polyclonal anti-p24 IgG antibodies as probes were used in a three-component sandwich assay (Figure 23). In a typical assay, the anti-p24 nanoarray was immersed in plasma samples containing HIV p24 protein (AIDS Clinical Trials Group Virology Laboratories Quality Assurance Program). The binding of p24 to anti-p24 IgG antibodies immobilized on the nanoarray was confirmed using AFM. The height profile showed an average height increase of 2.3 ± 0.6 nm (n=10).

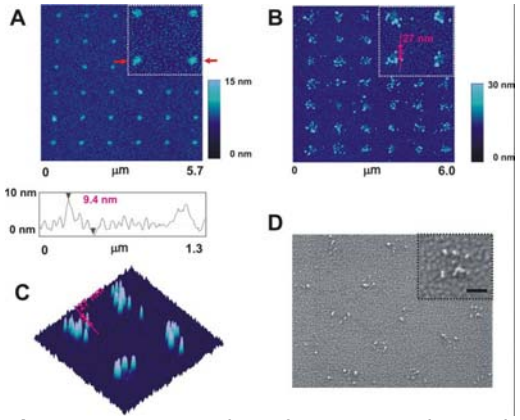


Figure 23. Detection of HIV p24 using anti-p24 nanoarrays. **(A)** Height profile of p24 binding to anti-p24 IgG. **(B-D)** p24 detection with anti-p24 IgG coated Au nanoparticles.

The signal resulting from the binding of p24 to the array could be amplified with gold nanoparticle probes functionalized with polyclonal antibodies to p24. A significant topography change (20.3 ± 1.9nm (*n*=10)) accompanied binding of the nanoparticles to the captured p24 molecules, which was consistent with a 1:1:1 reaction between monoclonal anti-p24 IgG absorbed onto the substrate, HIV p24 protein, and gold nanoparticles functionalized with polyclonal anti-p24 IgG. Anti-p24 nanoarrays incubated in control plasma samples without p24 protein, and probed with anti-p24 IgG gold nanoparticle probes showed no height increase for the anti-p24 features.

The applicability of this nanoarray-based immunoassay was accessed by screening plasma samples from HIV-infected (n = 8) and HIV-free (n = 10) men enrolled in the

Chicago component of the Multimember AIDS Cohort Study (MACS). 1 µL plasma samples from the 8 HIV–infected patients, and the 10 uninfected controls were analyzed in less than 6 hours. The AFM height profile verified p24 binding to anti-p24 IgG features and the anti-p24 IgG functionalized gold nanoparticles (Figure 23). Using this assay HIV p24 protein was found in plasma samples of HIV-1 infected men with less than 50 copies of RNA/ml plasma.

B.5. Synthesis of Metal Nanostructures Using DPN

B.5.1. Solid-State Nanostructures (Mirkin, Dravid)

A novel procedure was developed to fabricate solid-state metal nanostructures from DPN-generated templates. By applying a selective desorbing potential to a surface, a nanoscale gold template could be generated. Subsequently, different metal salts were electrochemically reduced and deposited onto the exposed gold surface. Using this approach Ag nanoarrays could be fabricated on a gold substrate (Figure 24). Interestingly, the resolution of the metal nanostructures fabricated by this method is only limited by the size of the DPN-generated features.

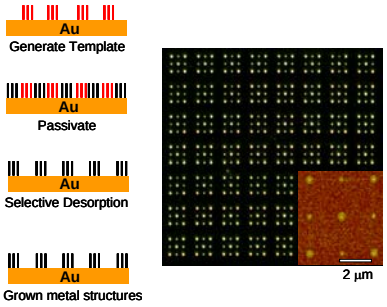


Figure 24. (A) Schematic of the fabrication procedure. **(B)** Darkfield optical micrograph of Ag nanostructures electrochemically grown on a thin film of Au. **Inset:** TM-AFM image of these nanostructures.

Progress was also made in using "precursor inks" for nanopatterning of inorganic and organic complexes. The conversion of precursors into appropriate structures can occur in three different ways: (a) polymerization during patterning via a water meniscus, (b) "*in-situ* or *in-process*" curing via an external stimulus such as UV exposure, and (c) thermo-chemical treatment after patterning, such as pyrolysis.

The site- and shape-specific patterning capabilities of DPN are particularly useful for the patterning of functional structures at specified locations, for example in-between patterned electrodes, to transport transduction signals. The rich and well-developed "bulk" sol-chemistries and synthesis protocols can be readily applied to DPN patterning. In particular, the site-specificity and serial patterning capability of DPN was used to fabricate an array of different SnO_2 sensor elements. A proof-of-concept detection scheme for a very sensitive, rapid response/recovery electronic nanonose is presented in Figure 25. This non-specific response to various gases can be used as reference "spectra" for toxic gas detection with pattern recognition procedures.

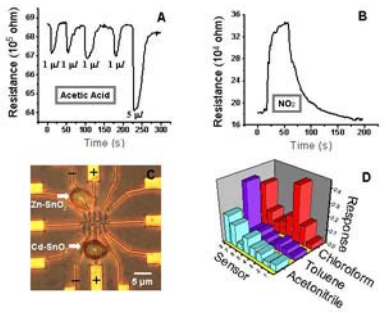


Figure 25. Electronic "Nanonose": Doped SnO_2 sensor elements directly patterned in-between electrodes. Sensing results for: **(A)** Acetic acid vapor and **(B)** NO_2. **(C)** Array of doped SnO_2 nanodisks, and **(D)** simultaneous detection of multiple gases via pattern recognition.

B.5.2. Fabrication of Nanowells (Mirkin)

DPN offers important advantages over other lithographic methods and allows one to fabricate structures of considerable flexibility

(Figure 26). It requires neither a master nor resist, and is therefore capable of rapid prototyping, which in turn allows one to implement complex patterns. The **Mirkin** group has developed a highly scalable technique to fabricate solid-state structures. This technique combines high-resolution DPN and electrochemical selective-desorption of organic monolayers to generate nanowells. When an array of cantilevers is used millimeter scale arrays of solid-state structures can be rapidly fabricated in less than 2 hours. Following the scheme outlined in Figure 26 a ten cantilever array was used to produce nanowells (Figure 27). The lateral resolution of this technique is determined by the original DPN pattern (30 nm). An important advantage of this method is that the well floor is chemically different from the well walls, which makes it possible to selectively functionalize the well-floor while keeping the walls intact. The depth of the wells is determined by the thickness of the gold film. Nanowells were generated on both Au and Ag surfaces with volumes as small as a few femtoliters.

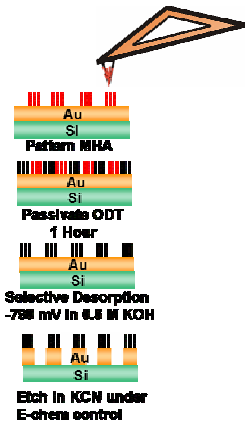


Figure 26. Schematic of the nanowell fabrication process

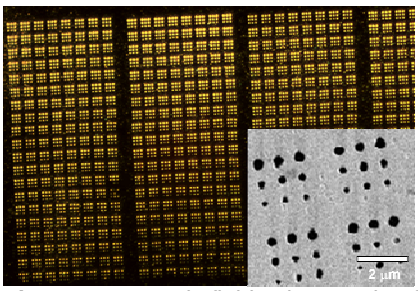
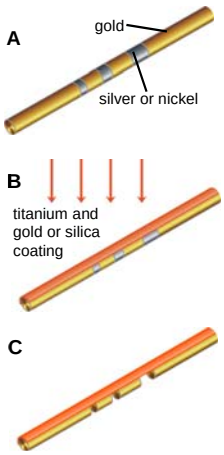


Figure 27. Dark field micrograph of nanowells etched into a 40 nm gold film. Inset: SEM image of a zoomed in section of the array.



Scheme 1. Fabrication of dented nanorods. **(A**) Striped metallic nanorods with alternating gold and silver or gold and nickel segments. **(B)** Top side of striped nanorods coated with titanium and gold or silica. **(C)** Released nanorods treated with etching solution.

B.5.3. Synthesis of Dented Metallic Nanowires by "On-Wire Lithography" (OWL) (Mirkin)

A novel, high-throughput, high-resolution technique called "on-wire lithography" (OWL) was developed for the lithographic processing of one-dimensional dented, metallic nanowires. This technique allowed us to fabricate routinely gap structures in the range of five to several hundred nanometers, which are ideal candidates for nanoelectronic and molecular electronic devices. In addition, multi-dented/gapped wire structures are promising candidates as plasmon wave guides and as surface enhanced Raman scattering substrates. OWL uses a combination of template-directed electrochemical synthesis of nanowires, electrochemical deposition, and wet-chemical etching. Single-gapped/dented wires were subsequently immobilized on microelectrodes and DPN was used to deposit different materials into the gap. OWL is based on the premise that it is feasible to synthesize segmented nanowires consisting of at least two types of materials, one susceptible and one resistant to wet-chemical etching. Following the scheme outlined in Scheme 1 Au-Ag and Au-Ni nanowires consisting of different segments could be successfully fabricated. The length of the segments could be tailored by controlling the charge passed during the electro-deposition process.

Dented nanowires are synthesized from striped metallic nanowires coated on one side of the wire surface with a controllable layer of metal or silica (Scheme 1). In a final step the active component, one of the stripes, is etched to yield dents or gaps, the width of which is controlled and can extend from the nm to micron range. Though other techniques are available for fabrication of this kind of gapped device, they allow synthesis of only one gap and have a low success rate. A key advantage of the OWL technique is its capacity to generate billions of gapped wires in one experiment without the need for sophisticated equipment or specially designed feedback systems.

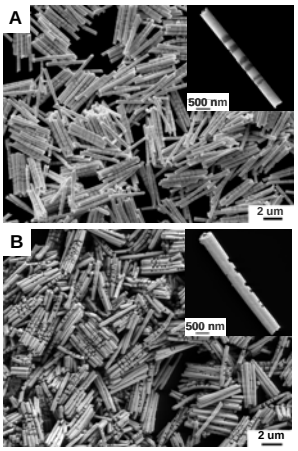


Figure 28. SEM images of nanorods: **(A)** striped metallic with alternating segments of gold and silver. **(B)** Dented with side coating of titanium and gold. Each rod is 4.5 µm long, with two 210 nm, two 140 nm, and two 70 nm dents (top to bottom).

In a typical experiment, striped metallic nanowires were prepared by electro-deposition of gold into porous anodic aluminum oxide (AAO) as described by Martin and co-workers. A thin, 200 nm layer of silver was evaporated onto one side of the AAO, which served as a cathode in an electrochemical cell with Ag/AgCl as a reference electrode, and a platinum wire as the counter electrode. The nanopores of the film were filled with Ag plating solution at a constant potential of -0.9 V vs. Ag/AgCl. Au and Ag were alternately deposited to form a structure like the one shown in Figure 28A. The segment length of these wires was controlled by monitoring the charge passed through the membrane. The Ag support and aluminum membranes were subsequently dissolved with concentrated nitric acid and sodium hydroxide solutions, and the physical dimensions and block composition of the wires measured by SEM (Figure 28 A and Figure 29).

In order to generate dented nanowires a basic protocol was followed. The wires were sonicated in water and dispersed onto a piranha treated hydrophilic glass slide. After drying the slides were coated with 10 nm titanium and 50 nm gold in a thermal evaporation. The coated wires were released from the slide by sonication, and the silver stripes removed with etching solution containing a 4:1:1 ratio of methanol:ammonia:hydrogen peroxide. The resulting structure is a dented nanowire as shown in Figure 28B. This basic protocol can be modified, and it allowed us to synthesize magnetic or insulated wires, if nickel was used as a sacrificial stripe or if the wires were coated with silica. The latter one is ideal for studying the electronic applications of the nanosized gap/dent.

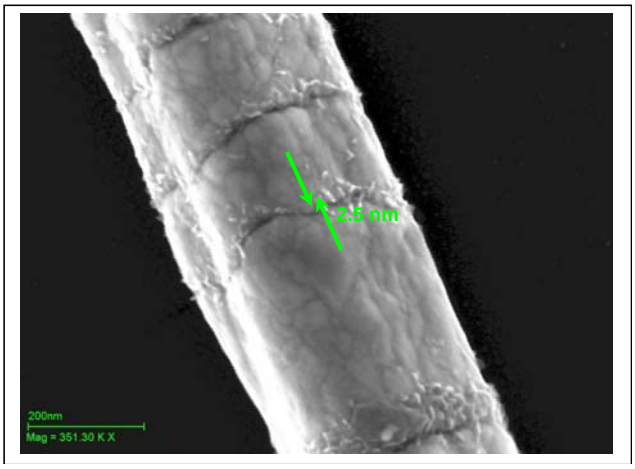


Figure 29. SEM image of a single nanowire with several gaps of 2.5 nm.

OWL has several unique applications. These are its capability to create stripes ranging from 2 nm to several microns. Second, the selective functionalizing of the wire surface before and after etching will allow us to create different surface properties (hydrophilic/hydrophobic) on the inside and outside of the gaps. Lastly this technique can be used to fabricate high-density disk/wire arrays from multi-striped nanowires by deposition of alternating layers of different metals.

C. Functional Materials for Data Storage, Sensing, and Diagnostics (Chandrasekhar, Dravid, Mirkin)

C.1. Inorganic Nanostructures (Dravid, Mirkin)

Nanostructures fabricated from inorganic and organometallic complexes are exceedingly useful structures that when compared to all-organic nanopatterns promise unique and complementary sensing/diagnostics properties. For example, magnetic, dielectric, ferroelectric, and catalytic nanostructures can be externally "addressed" without physically touching the nanostructure elements. Furthermore, when "tagged" with bio-recognition elements, inorganic nanostructures can provide useful and complementary capabilities for bio- or chemical sensing applications.

DPN-derived templates were used for the assembly of inorganic colloidal structures. Both magnetic and dielectric colloids could be directly assembled or patterned onto hydrophilic MHA DPN templates. In addition, sol-gels could be used as inks and patterned onto noble metal and oxide substrates. Through the choice of sol-gel precursor, tailored ceramic materials could be formed. The conversion of precursors to appropriate structures could occur in variety of ways: (a) polymerization during patterning via possible water meniscus, (b) "*in-situ* or *in-process*" curing via an external stimulus such as UV exposure, or (c) thermochemical treatment after patterning, such as pyrolysis.

The sol-gel precursor approach will open new avenues for the preparation of functional nanostructures for the development of sensing technology, data storage materials, and magneto/electronic devices. The site and shape-specific patterning capabilities of DPN were particularly useful as they allowed patterning of functional structures at specified locations. As an example, functional nanostructures could be deposited in-between patterned electrodes to form a complete circuit. The rich and well-developed "bulk" sol-chemistries and synthesis protocols could be readily applied to DPN patterning, and complex structures such as semiconductor oxide sensors (SnO_2, TiO_2), and the hard-magnet barium hexaferrite ($BaFe_{12}O_{19}$,) and optically active organic dyes have been successfully patterned.

C.2. High Sensitivity Miniature DPN-Derived Chemical Nanosensors (Dravid)

Our approach of patterning nanostructures via sol-gel inks was extended to a wide range of potential gas sensor materials including semiconducting oxides. Pristine and doped versions of SnO_2, ZnO, TiO_2 and ZrO_2, which are excellent candidates for gas sensor applications, were routinely patterned. The sol-gel based patterning of functional inorganic nanostructures has greatly facilitated fabrication of nanosensor elements composed of semiconducting oxides, which are proven macroscale chemical sensors. On the sub-100 nm scale, the oxide sensors have the potential to serve as sensors for gas with fast read-out, small volume requirement for chemicals, and easy integration with conventional micropatterned arrays. Miniaturized localized nanoscale sensor elements for semiconducting platinum doped tin oxide (Pt-doped SnO_2) sensors were manufactured

using DPN of appropriate sols in-between narrow electrode gaps. These sensors showed a fast response, rapid recovery, and low working temperature for carbon monoxide detection.

The ability of sol-gel inks to accept dopants and catalytic promoters in the solution phase greatly extends the ability to explore compositional phase space and to develop the most effective sensor composition. Furthermore, nanoporous sensor patterns and different promoter/dopant compositions made it possible to explore lower operating temperature ranges. Remarkable results with Pt-doped SnO_2 were obtained. Platinum (Pt) could be readily doped with sol-gel precursors, and patterned by DPN between pre-fabricated electrodes. When precursor inks doped with increasing amounts of Pt (2 %, 6 %, 10 %) were used, a dramatic change in the sensing behavior for a model toxic gas (CO) was observed. While the sensing performance for 10 % Pt-doped SnO_2 was low and flat at the usual operating temperature of 300-400ºC, the same composition performed exceptionally well at 75ºC (Figure 30).

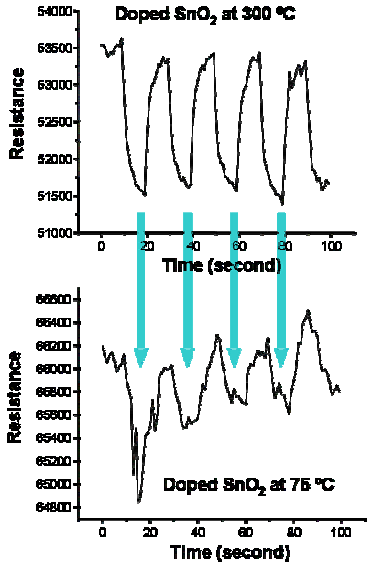


Figure 30. Comparison of the CO sensing behavior for 10 % Pt-doped SnO_2, at 300 ºC and 75 ºC.

In collaboration with Dr. Steve Semincik (NIST), the Dravid group has used DPN to pattern new sensor oxides on complementary metal oxide semiconductor (CMOS) microheater plates fabricated at NIST. This approach made it possible to heat locally individually-addressable sensor elements, and it allowed us to study different operating conditions such as base oxide, dopant, composition, and temperature when coupled with optimal sensor compositions.

The microstructure, chemical states, and adsorption properties of these nanostructured composites were investigated using a variety of analytical techniques including X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy/diffraction, electrical measurements, and temperature programmed desorption. Metallic Pt nanoparticles, Pt (IV) and loosely bound Pt-O species were identified in the annealed samples. The percolations of metallic Pt species in the semiconductor matrix reduced the overall resistance of the sample, and improved sensing.

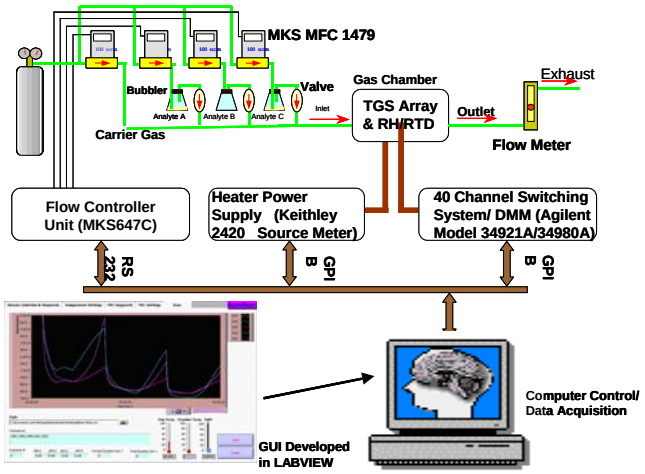


Figure 31. Schematic of the in-house developed experimental setup for gas sensing.

The DPN-derived inorganic nanopatterns were also extensively characterized using advanced microscopy techniques to ensure their local structure, chemistry and overall identity.

This was accomplished by DPN patterning of inorganic structures on ultra-thin Sin membranes for direct imaging in TEM. Sol-gel derived DPN nanostructures of inorganic sensor elements exhibit an ultra fine grain size, but maintain appropriate stoichiometry and overall structure.

An integrated and unified testing system for high-throughput and accurate, sensitive, and reproducible analysis for gas sensing was developed in-house (Figure 31). This system incorporates DPN-derived sensor elements combined with software developed in-house and hardware modules. Our software analysis protocol was able to decipher subtle changes in sensing behavior, and could accurately discriminate various VOCs (volatile organic compounds) under practical conditions.

C.3. Fabrication of Nanoelectrodes and Biosensory Devices (Dravid, Mirkin)

Three distinct techniques were developed for the fabrication of nanometer scale gaps in metallic electrodes. These were: Two-angle evaporation, electromigration, and electrochemical deposition.

Two-angle evaporation: Electron beam- lithography was used for writing on a PMMA bilayer to create a suspended PMMA bridge. Precision angle evaporation from two angles was then used to control the width of the nanogaps.

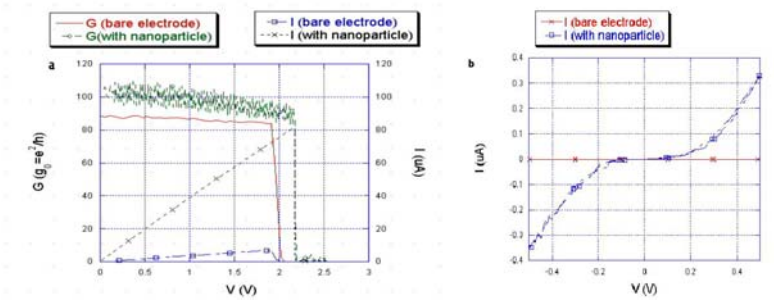


Figure 31. (a) G (conductance) and I (current) vs. V (voltage bias) during junction break. **(b)** I-V characteristic of Au nanoparticles modified by hexanedithiol. Control sample for **(a)** and **(b)**: bare electrodes

Electromigration uses e-beam lithography to fabricate a microbridge, which is a short, narrow metallic wire between two large electrodes. To measure organic molecules, the metallic regions of the sample were coated with the molecule of interest, and a dc voltage bias applied that was slowly increased. Under dc voltage bias, the microbridge eventually broke at its weakest point, and produced a small nanometer scale gap that could be bridged by one or two organic molecules. Figures 31 (A) and (B) show the conductance of a microbridge during the electromigration process. The resulting current-voltage (I-V) characteristics with and without the organic molecule, which in this case is hexanedithiol, bridge the gap. The current in samples without hexanedithiol does not change with increasing bias, and the I-V characteristic of the sample with the organic molecule is clearly non-linear, with a threshold of about 0.2 V.

Electrochemical deposition: The possibility of narrowing the gaps through electrodeposition gold nanoelectrodes fabricated by e-beam fabricated was explored. The electrodeposition was carried out in a solution of ($KAu(CN)_2$). Figure 32 shows an example of the resulting electrode structure with a gap on the order of only a few nanometers, and the I-V characteristic of an electrodeposited device bridged with gold nanoparticles modified by DNA. The experiment was conducted at 4K using the cryostat

and electrical transport device provided by the Mirkin Group. The I-V characteristics depicted in Figure 32 provided evidence of Coulomb blockade of charge.

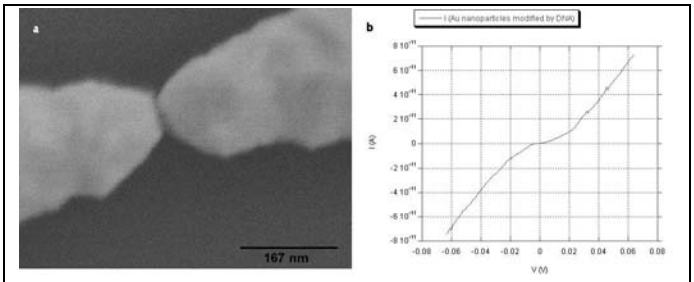


Figure 32. (a) SEM image of nanoelectrodes fabricated by electrochemical deposition. **(b)** I-V characteristic of Au nanoparticles modified by DNA.

C.4. Fabrication of Conducting Polymer Nanostructures via DPN (Mirkin, Dravid)

Conducting polymers are an attractive alternative for a range of applications, including sensors for explosive materials. Controlled patterning of conducting polymers is essential for such applications. The **Dravid** group has developed an acid-promoted polymerization method for direct DPN patterning of conducting polymers. The reactive liquid precursors polymerize and generate solid products after patterning as in sol-gel transitions. Using this technique conducting polymers formed from pyrrole and tetrahydrofuran could be successfully patterned. In fact, this made it possible to produce very fluidic or viscous (sticky) inks for effective patterning at the nanoscale. The conducting polymers were simultaneously doped by acid added to the system as a catalyst, and upon solidification, they displayed high conductance and crystalline structures. Miniaturized conducting polymer devices capable of light sensing were fabricated by DPN patterning using the proposed monomer ink (Figure 33).

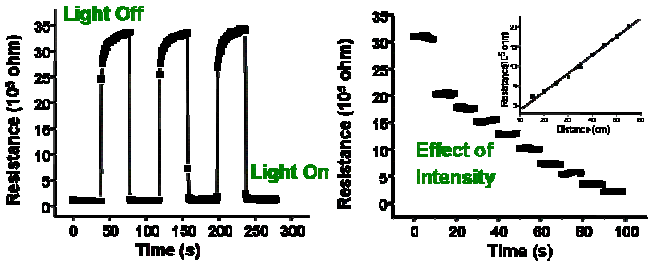


Figure 33. Photo-sensing properties of DPN-derived conducting polymer nanopatterns, trapped in-between electrodes. The patterns are sensitive to not only light (left) but its intensity (right)

Stable nanoscale conducting polymer features were fabricated by DPN on semi-conducting and metallic substrates. The driving force for ink transport to the surface was the electrostatic interaction between the water soluble conducting polymer inks and the charged substrates. Furthermore, nanoscale sulfonated poly-aniline (SPAN) conducting polymer devices were generated by e-beam and microfabricated metallic electrode arrays (Figure 34). The current-voltage characteristics of the conducting polymer device displayed a highly nonlinear behavior, which is entirely different from the bulk conducting polymer. Differential conductance measurements, which are

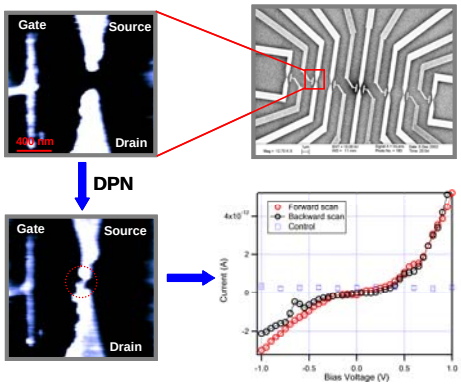


Figure 34. Fabrication of doped SPAN conducting polymer devices via DPN. **(Left)** AFM image of the SPAN polymer nanostructure before and after DPN. **(Right)** Current-voltage (I-V) characteristics of SPAN polymer device at room temperature.

proportional to the density of states (DOS) of the device, show interesting features at various temperatures, which are characteristic for such nanoscale devices and are likely due to finite size effects.

C.5. Multiplexed Localized Patterning of Polymers (Dravid)

Usually conducting polymers are synthesized from appropriate monomers by chemical or electrochemical oxidative polymerization in solution, and patterned on substrates by screen or inkjet printing, stamping, traditional lithography (photo, electron, and ion beam lithography), or emerging technologies such as scanning probe lithography, soft lithography, or electrochemical methods. An alternative patterning strategy uses monomers as building blocks and exploits polymerization within a spatially restricted volume or at specific locations on a substrate. For the large-scale production of miniaturized complex architectures, it should ideally be possible to pattern at low cost multiple materials at specific locations with high efficiency and resolution, and accurate positioning. **Dravid** has developed and utilized a monomer vapor-based approach capable of large scale patterning of multiple conducting polymers via electric-field-induced polymerization. This method facilitated polymerization in between individually addressable electrodes. Using this approach the precise registry of patterned structures and electrodes is not necessary. Using different monomer vapors, various conducting polymers could be patterned between localized electrode gaps. In principle, the number of patterns produced in one run can be very large provided that sufficient electrode gaps and means to address them are available. This simple and robust method is highly compatible with the microelectronics technology and represents significant progress in the controlled patterning of multiple polymers.

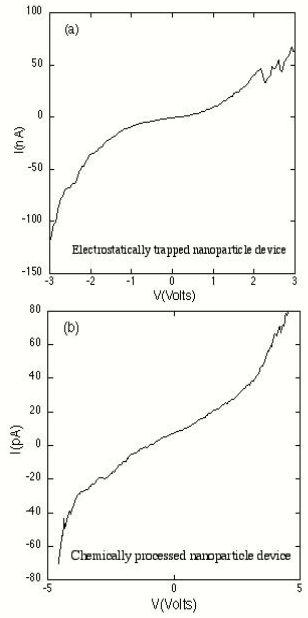


Figure 35: Comparison of the IV characteristics of devices produced by **(A)** electrostatic trapping, and **(B)** chemical processing at room temperature.

C.6. Electrical Properties of Nanostructures (Chandrasekhar)

Two different techniques were used to fabricate gold nanoparticles coated with organic material, typically DNA. Both techniques started with metallic nanogaps patterned in-house using the e-beam lithography. The patterned devices had gaps ranging from 100 nm to less than 5 nm between the gold electrodes. The first technique used the devices with the larger gaps. Using electrodeposition the gaps were first reduced in size to 10-20 nm, followed by functionalization of the gold electrodes, which was done by dipping the gold electrodes into a solution of suspended gold nanoparticles coated with the oligonucleotide sequence of the anthrax lethal factor of *Bacillus anthracis*. For samples with a narrower gap size, the electrodeposition step could be skipped.

The second technique used narrower gap electrodes to electrostatically trap the gold nanoparticles by placing a small drop of the solution of suspended nanoparticles on top of the electrodes,

followed by application of a high-frequency (~MHz) voltage across the device. This method traps only a few nanoparticles between the electrodes, since the trapping process is self-terminating. As soon as a nanoparticle bridges the gap, the voltage across the device drops, and terminates the trapping process. In general, the number of nanoparticles trapped between the electrodes depended on the ratio of the gap width to the particle diameter. In order to trap one particle, gaps of less than 15 nm are needed.

Devices fabricated by the two techniques demonstrated single-electron charging effects, even at room temperature, but showed one major difference. Figure 35 shows the IV characteristics of two samples, one produced by electrodeposition and functionalization, the second one by electrostatic trapping. Although the curves look similar, the current of the device fabricated by electrostatic trapping is approximately three orders of magnitude larger than the current of the other device. The reason for this difference in unknown, but is believed to be due to differences in the ambient environment during fabrication, and the time between fabrication and measurement.

D. Development of Models and Computational Tools for Self-Assembly (Ratner, Schatz)

D.1. Surface Diffusion Modeling (Schatz)

Binary alkylthiol solutions form on gold substrates self-assembled monolayers (SAMs) that are composed of one kind of alkylthiol and that can have domain structures of up to 20 nm in size. In solution the natural growth of SAMs and their domain size can only be controlled kinetically, but a new nanoengineering technique, called nanografting, allows one to exert direct control of nanoscale patterning at the molecular level using an AFM tip in solution. Nanografting uses an AFM tip to displace adsorbed thiol molecules from a naturally grown monolayer during immersion in the same binary thiol solution (Figure 36). As a result new molecules will self-assemble onto the freshly exposed surface. The homogeneity of the nanografted area can be controlled through the speed of the tip (from0.01~10 μm/s). A more slowly moving tip induces a more homogeneous pattern.

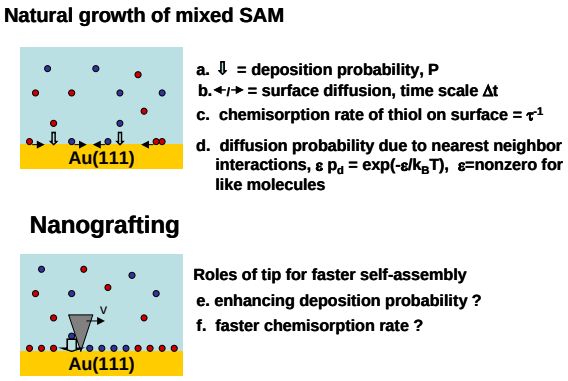


Figure 36. Modeling of natural growth and nanografting.

In order to understand the roles of (1) surface diffusion of the thiol molecules in naturally growing domains, and (2) the AFM tip in the nanografting process, Monte Carlo simulations were performed. The natural growth of the monolayer was modeled assuming that thiol molecules will arrive at the surface at a constant rate (P), and will undergo surface diffusion (diffusion time scale Δt) until they are chemisorbed (chemisorption rate τ^{-1}). Stronger interactions between the same kinds of molecules were accounted for by assuming that diffusion away from the same kind of nearest neighbor is less frequent, and that the deposition probability is higher for the surface area immediately behind the moving AFM tip.

Modeling experiments conducted under these assumptions allowed us to conclude that at slow tip speeds homogeneous monolayers will be formed, whereas at fast tip speeds larger domain are created. These results are similar to what is found experimentally.

A lattice of 100×100 needs to be used to observe domain structures of up to 20 nm in size. These domain sizes can be found in experiments that use a lattice spacing of 5 Å. To estimate simulation parameters from a kinetics study of mM solutions, the deposition rate has to be in the order of 1 sec^{-1}. Assuming a surface diffusion time scale in the range of nsec to μsec, the deposition probability for a unit simulation time will be 10^{-9} to 10^{-6}. Since the chemisorption rate τ^{-1} cannot be determined easily experimentally, and the nearest neighbor interactions ε between physisorbed thiol molecules are unknown, our simulations contain three variables. To interpret the physical importance of these three processes for the observed domain structures and sizes, it needs to be determined which parameter values are appropriate. Figure 37 displays the results of a modeling experiment of a 201×201 square lattice, which allowed us to conclude that the longer lifetime of physisorbed states leads to bigger domains.

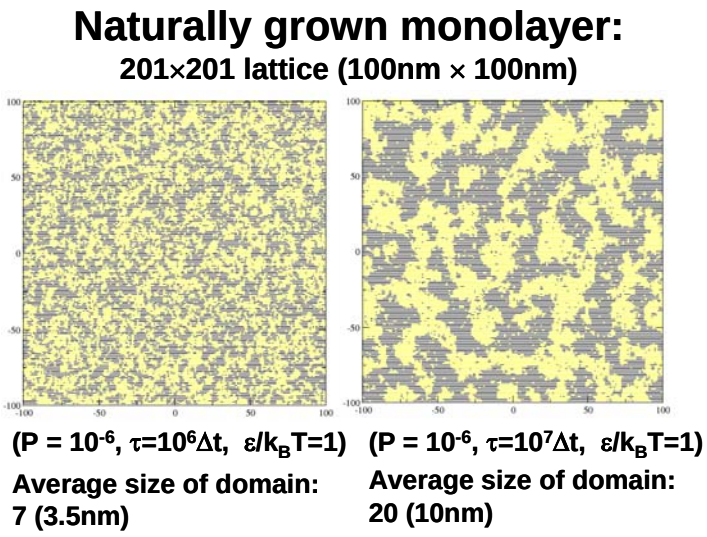


Figure 37. Dependence of domain size on chemisorption rate τ^{-1}

D.2. Surface Adhesion Modeling (Schatz)

Surface electronic structure calculations were applied to investigate how the amino acid DOPA, an important component in bio-adhesives, adheres to titanium oxide surfaces. These modeling experiments, based on cluster models containing one or two titanium atoms, allowed us to calculate the reaction energy needed for the formation of bidentate and monodentate structures with catechol, which serves as a model for DOPA. For these modeling experiments two cluster models were used to study different absorption sites on the TiO_2 surface: (a) a titanium atom coordinated to five oxygen atoms via a Ti-O single bond, and (b) a titanium atom coordinated to five oxygen atoms, one of these corresponding to a Ti=O double bond. In addition to these two models, different ones assuming one- and two-titanium atom models of the surface have been considered. Both Hartree-Fock and Density Functional Theory calculations using a 6-31G* basis set were carried out. These calculations allowed us to conclude that a) bidentate structures are favored over monodentate structures by around 5 kcal/mol, and that b) the binding energy of the bidentate structure is around 25 kcal/mol, a number that correlates well with unpublished results generated by our collaborators at Northwestern.

D.3. pH/Salinity Phase Diagrams for Self-Assembling Peptide Amphiphiles (Ratner)

The **Ratner** group has extended its studies of the impact of environmental factors on the shape and properties of supramolecular nanostructures composed of peptide amphiphiles (PA), and expanded these studies to include the full range of pH and salinity conditions that are potentially important for future experiments and medical applications of these agents. Modeling studies that assumed a reduced geometric model demonstrated that PA molecules will not assemble into supramolecular structures at low pH and salt concentrations. At higher salt concentrations, however, spherical micelles will form. These modeling experiments also revealed potential phase transitions between cylindrical and spherical micelle structures

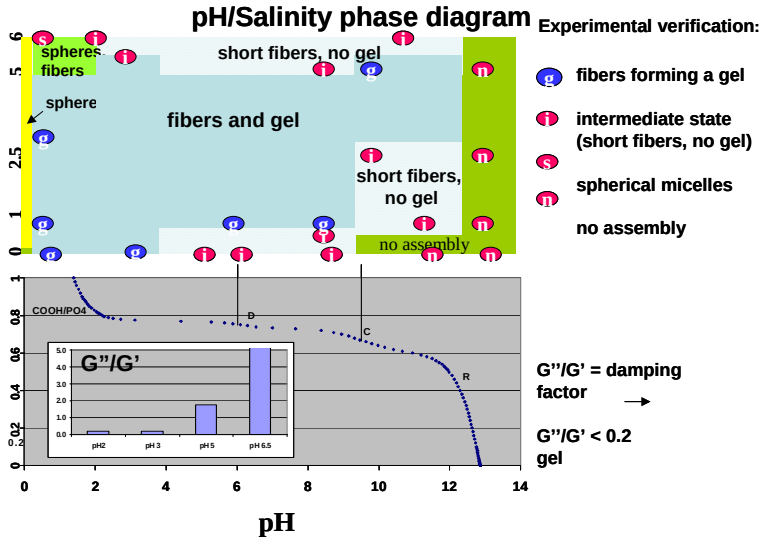


Figure 38: pH/Salinity phase diagram. The titration curve of the peptide-amphiphile and the damping factor G"/G' is shown in the inset.

Force field molecular dynamics simulations at high pH values illustrated that the stability of the cylindrical micelles depends on the salinity of the solution (Figure 38). These simulations proved very clearly that micelles will dissemble at low salinity. Higher salt concentrations on the other hand stabilize the cylindrical formation. It could also be established that a slight increase in the salinity of the solution will stabilize the cylindrical fibers at physiological pH.

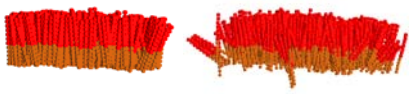


Figure 39. **Self-assembled Au/PPy nanorods.** The configuration on the **left** represents the initial state of amphiphiles in a matrix, 100 nm apart. This configuration on the **right** results from a similar matrix in which the amphiphiles are 200nm apart. The stability and curvature of the two assemblies are different due to different starting conditions, and are thus kinetically controlled.

D.4. Self-Assembly of Mesoscopic Au/PPy Amphiphiles (Ratner)

In addition to the aforementioned studies of self-assembling peptide amphiphiles (PA) the **Ratner** group has undertaken a second project that uses mesoscopic Au/PPy amphiphiles**,** a particular kind of amphiphiles created in the **Mirkin** lab. Mesoscopic Au/PPy amphiphiles will form vesicular structures with a higher curvature than expected based on our understanding of the geometric packing constraints controlling self-assembly of these structures. As a result of these studies the hypothesis was developed that these

assemblies are kinetically controlled. This hypothesis concurred with experimental findings that these molecules assemble into higher order structures only under very specific conditions. Monte Carlo simulations confirmed our hypothesis, and suggested in addition new ways of stabilizing and extending the range of such assemblies.

3. PERSONNEL SUPPORTED

Postdocs:	**% of salary provided by the grant:**	
Nurit Ashkenasy (Ghadiri)	63 %	(2001-2005)
Raquel Martin (Kaplan)	100 %	(2001-2002)
Amarjit Singh (Kaplan)	10 %	(2002-2003)
Irene Tsai (Kaplan)	50 %	(2004-2005)
Jung-Hyurk Lim (Mirkin)	60 %	(2001-2004)
Hua Zhang (Mirkin)	100 %	(2001-2003)
Shouwu Guo (Mirkin)	100 %	(2002-2003)
Max Ovchinnikov (Mirkin)	88 %	(2002-2004)
Sang Woo Han (Mirkin)	60 %	(2002-2003)
Yi Zhang (Mirkin)	100 %	(2002-2003)
Seung Woo Lee (Mirkin)	90 %	(2003-2005)
Ling Huang (Mirkin)	65 %	(2003-2005)
Yu-Hsu Chang (Mirkin)	25 %	(2004-2005)
Alexander Burin (Ratner)	25 %	(2001-2002)
Vance Wong (Ratner)	50 %	(2002-2004)
Alessandro Troisi (Ratner)	25 %	(2002-2004)
Joonkyun Jang (Ratner & Schatz)	100 %	(2001-2003)
Stefan Tsonchev (Ratner)	100 %	(2003-2005)
Irina Paci (Ratner)	50 %	(2004-2005)
Stefan Tsonchev (Ratner&Schatz)	100 %	(2002-2003)
Stefan Tsonchev (Schatz)	100 %	(2001-2002)
Joonkyun Jang (Schatz)	100 %	(2003-2004)
Seol Ryu (Schatz)	100 %	(2003-2005)
Jeffrey D. Hartgerink (Stupp)	50 %	(2001-2002)
Liang-Shi Li (Stupp)	42 %	(2003-2004)
Graduate Students:		
Nathan Gianneschi (Mirkin)	100 %	(2001-2003)
Ki-Bum Lee (Mirkin)	39 %	(2001-2004)
Xiaogang Liu (Mirkin)	100 %	(2001-2002)
Jwa-Min Nam (Mirkin)	100 %	(2001-2003)
Aaron Brown (Mirkin)	100 %	(2002-2003)
Khalid Salaita (Mirkin)	60 %	(2002-2005)
Raymond Sanedrin	75 %	(2003-2004)
Lidong Qin (Mirkin)	25 %	(2004-2005)
Meisa Khoshbin (Mirkin)	25 %	(2004-2005)
Donna Wilson (Kaplan)	33 %	(2001-2003)
Peng Xu (Kaplan)	100 %	(2001-2005)
Jia Huang (Kaplan)	38 %	(2002-2003)

Amarjit Singh (Kaplan)	20 %	(2003-2004)
Ming Su (Dravid)	100 %	(2001-2004)
Zixiao Pan (Dravid)	0 %	(2003-2004)
Suresh Donthu (Dravid)	43 %	(2003-2005)
Keith Wilcoxen (Ghadiri)	50 %	(2001-2002)
W. Seth Horne (Ghadiri)	0 %	(2002-2005)
David Vodak (Ghadiri)	0 %	(2002-2003)
Zhengfan Zhang (Chandrasekhar)	63 %	(2001-2003)
Zhang Yu (Chandrasekhar)	100 %	(2002-2003)
Linlin Zhao (Schatz)	50 %	(2004-2005)
Benjamin Messmore (Stupp)	100 %	(2001-2004)
Heather Berger (Stupp)	100 %	(2001-2002)
Hongzhou Jiang (Stupp)	100 %	(2001-2005)
Steve Bull (Stupp)	42 %	(2002-2003)
Mustafa Guler (Stupp)	42 %	(2002-2003)
Marina Sofos (Stupp)	42 %	(2002-2003)
Heather Behanna (Stupp)	33 %	(2002-2003)
Krista Niece (Stupp)	33 %	(2002-2003)
Dhruv Dayal (Stupp)	25 %	(2002-2003)
Eli Sone (Stupp)	17 %	(2002-2003)
Wen-Wen Tsai (Stupp)	75 %	(2003-2004)
Lorraine Hsu (Stupp)	42 %	(2003-2004)
David Coffey (Ginger)	0 %	(2003-2004)
Andrea Munro (Ginger)	0 %	(2003-2004)

Undergraduate Students:

Travis Harper (Dravid)	0 %	(2001-2002)
Aroop Chatterjee (Dravid)	0 %	(2002-2003)
Nora Colligan (Dravid)	0 %	(2003-2004)
Darrius Guiden (Dravid)	0 %	(2003-2004)
Jacqueline Romero (Higgins/Mirkin)	100 %	(2001-2002)
Agbeko Komla (Schatz)	100 %	(2001-2002)
Jacqueline Roy (Kaplan)	0 %	(2001-2002)
Cona Anwar (Kaplan)	0 %	(2002-2003)
Andrew Cai (Kaplan)	10 %	(2004-2005)
Joe Schipani (Kaplan)	10 %	(2004-2005)
Peter Salveson (Ginger)	0 %	(2003-2004)
Ryan Thompson (Ginger)	0 %	(2003-2004)

Visiting Faculty/Scientists:

Regina Valluzzi (Kaplan)	0 %	(2002-2003)
Peggy Cebe (Kaplan)	0 %	(2002-2004)
Mark Cronin-Golomb (Kaplan)	0 %	(2002-2003)
Thomas Thundat (ORNL, Dravid)	0 %	(2002-2004)
Fred Arnold (Schatz)	10 %	(2003-2004)
Baudilio Tejerina (Schatz)	5 %	(2004-2005)

4. PUBLICATIONS

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B. Books and/or Book Chapters

1. Mirkin, C.A.; Demers, L.M.; Hong, S. "Dip-Pen Nanolithography: Direct Writing of Soft Structures on the Sub-100-Nanometer-Length Scale," in Direct-Write Technologies for Rapid Prototyping Applications. Eds. Alberto Pique and Douglas B. Chrysey, Academic Press, Boston **2001**, 303-312.

2. Stupp, S.I.; Beniash, E.; Hartgerink, J.D.; Sone, E.D. "Self-Assembling and Biomimetic Biomaterials" in *Bio-implant Interface: Improving Biomaterials and Tissue Reactions*; CRC Press: Boca Raton, **2003**, 393-406.

C. Proceeding Articles

1. Xu, P.; Kaplan, D.L. "Horseradish Peroxidase Catalyzed Polymerization of 4-Aminothiophenol on Surfaces via Dip-Pen Nanolithography" Polymer Abstract and Preprint, ACS Annual Meeting, New Orleans, 2003.

2. Bullen, D.; Chung, S.W.; Wang, X.; Zou, J.; Liu, C.; Mirkin, C.A. "Development of Parallel Dip-Pen Nanolithography Probe Arrays for High Throughput Nanolithography," *Proceedings of the MRS,* **2002***, 758,* LL4.2.1-LL4.2.10.

5. INTERACTIONS

A. Presentations/Presentations at Meetings, Conferences, Seminars

Dravid

2004 Americas Materials Conference: Chile, US and Brazil, Santiago, Chile: "Towards Novel Nano-Biosensors."

2004 University of Wisconsin, Milwaukee, WI: "Site-Specific Nanopatterning of Inorganics: Nanodots and Microcantilevers."

2004 University of Buenos Aires, Argentina: "Nanostructures for Biochemical Nanosensors."

2004 MRS Spring Meeting, San Francisco, CA: "Site-Specific Nanopatterning of Inorganics."

2004 AFOSR DPN Workshop, Duck Key, FL: "Teaching Old Materials New Tricks: Site- and Shape Specific Nanopatterning."

2004 Argonne National Lab, Bio-Division Colloquium Series Seminar, Argonne, IL: "Emerging Paradigm in Biochemical Sensing via Nanostructured Materials."

2004 University of Pennsylvania, MSE Department Colloquium Seminar Series Philadelphia, PA: "Site- and Shape-Specific Nanopatterning of Inorganics."

2004 Virginia Commonwealth University, Colloquium Seminar Series, Richmond, VA: "Emerging Paradigms in Bio-Nanosensors."

2004 University of Buenos Aires, Buenos Aires, Argentina: "Nanostructures for Bio-Chem Nanosensors."

2004 MRS Spring Meeting 2004, San Francisco, CA: "Site-Specific Nanopatterning of Inorganics."

2003 Annual MRS Meeting, Boston, MA: "Site- and Shape Specific Nanopatterning of Ferroelectrics", "Miniaturized Electronic Nanonose."

2003 Indian Institute of Technology, Institute Lecture Series, Bombay, India: "Emerging Issues in Nanoscience and Nanotechnology," "Advanced Electron Microscopy of Interfaces and Defects."

2003 Brazilian MRS Bi-Annual Meeting, Rio de Janeiro, Brazil: "Nanopatterning of Inorganics."

2003 Integrated Nanosystems Meeting, Palo Alto, CA: "Nanopatterning."

2003 Annual Microscopy Meeting, San Antonio, TX: "Nanopatterning."

2003 University of California, Santa Barbara, CA, Seminar: "Nanopatterning of Inorganics."

2003 IBM Watson Research Center, NY: "Teaching Old Materials News Tricks: Nanopatterning of Functional Inorganics."

2003 American Ceramic Society, Annual Meeting, Nashville, TN: "Electronic Nano-Nose: Patterned Semiconducting Oxide Sensors."

2003 University of Buenos Aires, Buenos Aires, Argentina: "Nanotechnology at the Organic/Inorganic Interface."

2003 JEOL Corp., Tokyo, Japan: "Nanotechnology and Nanoanalysis at Northwestern."

2003 Annual Meeting of Microscopy and Microanalysis, San Antonio, TX: "Nanoanalysis of Nanopatterns."
2002 MSE Department Colloquia, UIUC, Urbana, IL: "Inorganic Nanopatterning."
2002 International Conference on Inorganics, IIT Bombay, India: "Inorganic/Organic Complexes via Dip-Pen Nanopatterning."
2002 Delft University, Netherlands: "In-Situ Microscopy and Nanomanipulation."
2002 JEOL Corporation, Tokyo, Japan: "Role of Electron Microscopy in Nanotechnology."
2002 NIH, Bethesda, MD: "Bio-Nanopatterning: Towards Single-Molecule Sensing."
2002 ETH, Department of Chemistry, Zuerich, Switzerland: "Optically Active Nanopatterning."
2002 Max-Planck Institute, Stuttgart, Germany: "Electron Microscopy of Nanostructures."
2002 Lehigh University, Short Courses, Bethlehem, PA: "Characterization of Nanostructured Materials."
2002 Gordon Research Conference, Meriden, NH: "Teaching Old Ceramics New Tricks: Site-Specific Nanopatterning of Functional Inorganics."
2002 University of Illinois at Urbana-Champaign, IL: "Site- and Shape-Specific Nanopatterning of Ceramics."
2002 PASI, Joint Argentina-NSF Workshop on Ferroelectrics, Rosario, Argentina: "Nanopatterning of Addressable Functional Inorganic Nanostructures."
2001 MRSEC Director's Meeting, Brown University, Providence, R.I.: "Synthesis, Patterning, and Microscopy of Nanostructures."
2001 University of Connecticut, Department of Materials Science and Engineering, Colloquium, Storrs, CT: "Development and Management of Shared User Facilities."
2001 IIT Bombay, India: "Microscopy for Nanotechnology and Vice Versa."

Ginger

2004 French-US Conference on Molecular Electronics, Paris, France: "Bridging 'Top Down' and 'Bottom Up' Assembly."
2004 ACS National Meeting, Philadelphia, PA, Invited Seminar: "Controlling Phase Separation in Conjugated Polymer Blend Films with Nanolithographic Templates."
2004 ASME Nano Training Bootcamp, Evanston, IL: "Principles of Self-Assembly".
2004 ACS Northwest/Rocky Regional Meeting, Logan UT: "Templated-Directed Assembly of Nanostructured Organic Films."
2004 DURINT Biomimetics Seminar, University of Washington, Seattle, WA: "Bridging 'Top Down' and 'Bottom Up' Assembly."
2004 AFOSR DPN Workshop, Duck Key, FL: "Dip-Pen Nanolithography for Nanoscale Biosensing and Optoelectronic Studies."
2003 University of Washington, Seattle, WA: Condensed Matter Physics Seminar "Quantum Dots, Diodes and DNA."
2003 University of Washington, Seattle, WA, Nanotechnology Seminar Series: "From Nanoparticles to Nanolithography."

Kaplan

2003 University of Massachusetts, Lowell Annual Symposium, Boston, MA: "Biocatalytic Reactions Carried out by DPN."
2002 Emory University, Atlanta, GA: "Fibrous Proteins."
2002 University of California, Santa Barbara, CA: "Fibrous Proteins."
2002 AiChE Annual Meeting Presentation: "Collagen Assembly."
2002 Naval Research Laboratory: "Self-Assembly."
2002 University of Wyoming, Bozeman, WY: "Fibrous Proteins."
2001 Wright Patterson AFB, Materials Group, OH: "Fibrous Proteins Seminar."

Mirkin

2005 Nanoscience Seminar Series, duke University, Durham, NC: Massively Parallel Dip-Pen Nanolithography," Synthetic Supramolecular Allosteric Catalysts."
2005 228th ACS national Meeting, San Diego, CA: "Anisotropic Nanostructures: Synthesis, Assembly, and Function," "Bio-Barcode Assay: PCR-like Sensitivity for Proteins, Nucleic Acids, and Small Molecules."
2005 AACC Oak Ridge Conference, Baltimore, MD: "The Bio-Barcode Assay: Towards PCR-like Sensitivity for Proteins, Nucleic Acids, Small Molecules, and Metal Ions."
2005 Princeton University, Princeton, NJ: "Encoded Nanostructures for Use in Biodiagnostics."
2005 BIOMEMS Seminar, Boston, MA: "Bio-Barcode Assay: PCR-like Sensitivity for Proteins, Nucleic Acids, and Small Molecules."
2005 Gordon Research Conference: 3Chem of Supramolecules, Colby College, ME: "Supramolecular Allosteric Catalysts."
2005 Gordon Research Conference: Bioorganic Conference, Andover, NH, 2005, "The Bio-Barcode Assay: Towards PCR-like sensitivity for Proteins."
2005 AFOSR Biomimetic Program, San Diego CA: "Ultrasensitive and Selective Chip Based Detection of DNA."
2005 Nanoscience Seminar Series, Duke University, Durham NC: "Massively Parallel Dip-Pen Nanolithography," "Synthetic Supramolecular Allosteric Catalysts."
2004 227th ACS National Meeting, Anaheim, CA: "Building Nanotech Companies in a University Environment," "DNA-mediated Assembly of Nanostructured Materials: Structure, Properties, and Biodetection Applications."
2004 MRS Spring Meeting, San Francisco, CA: "Self-Assembly of Mesoscopic Amphiphiles," "Combinatorial Nanotechnology through Massively Parallel DPN," Ultrasensitive and Multiplexed Protein Detection with Nanoparticle-based Bio-Barcodes."
2004 NIAID Bio-defense Workshop, Bethesda, MD: "Nanostructures in Biodiagnostics: Will They Make a Difference?"
2004 Gordon Research Conference: Bioanalytical Sensors, Oxford, UK: "Bimolecular Detection with Bio-barcodes: PCR-Like Sensitivity for Proteins, DNA, RNA, and Small Molecules."
2004 Zizith International Symposium on Supramolecular Chemistry, Notre Dame, IN: "Synthetic Supramolecular Allosteric Catalysts."

2004 Beckman Symposium, Irvine, CA: "Tools and Methods That Will Fuel the Nanotechnology Revolution."

2004 AVS 51st International Symposium, Anaheim, CA: "The Bio-barcode Approach to Detecting DNA, Proteins, and Small Molecules."

2004 MRS 2004 Fall Meeting, Boston, MA: "Massively Parallel Dip Pen Nanolithography."

2004 NIAID Biodefense Workshop, Bethesda, MD: "Nanostructures in Biodiagnostics: Will They Make a Difference?"

2004 Gordon Research Conference: Bioanalytical Sensors, Oxford, UK: "Biomolecule Detection with Bio-barcodes: PCR-Like Sensitivity for Proteins, DNA, RNA, and Small Molecules."

2004 XIIIth International Symposium on Supramolecular Chemistry, Notre Dame, IN: "Synthetic Supramolecular Allosteric Catalysts."

2004 Korean Universities/Physical Society Series, Seoul, Korea: "Nanostructures in Biodiagnostics: A New Frontier in Medicine," Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology," "Encoded Nanostructures for the Detection of Biomolecules."

2004 NanoBio Summit, Cleveland, OH: "The Bio-Bar Code Assay: Towards PCR-like Sensitivity for Proteins, Nucleic Acids, Small Molecules, and Metal Ions."

2004 BioNano Conference, London, UK: "The Bio-Bar Code Assay: Towards PCR-like Sensitivity for Proteins, Nucleic Acids, Small Molecules, and Metal Ions."

2004 DARPA Advanced Lithography Program Review, Las Vegas, NV: "Massively Parallel Dip Pen Nanolithography."

2004 227th ACS National Meeting, Anaheim, CA: "Building Nanotech Companies in a University Environment," "DNA-mediated Assembly of Nanostructured Materials: Structure, Properties, and Biodetection Applications."

2004 MRS 2004 Spring Meeting, San Francisco, CA: "Self-Assembly of Mesoscopic Amphiphiles," "Combinatorial Nanotechnology through Massively Parallel DPN," "Ultrasensitive and Multiplexed Protein Detection with Nanoparticle-based Bio-barcodes."

2004 NSF Workshop "Japan – US Symposium on Directed Self-Assembly and Self-Organization" Santa Barbara, CA: "Self-Assembly of Anisotropic Structures."

2004 AFOSR 2312 DX Program Review, Hawk's Cay, FL: "Surface-Templated, Bio-Inspired Synthesis and Fabrication of Functional Materials," "Ultra-sensitive and Selective Chip-Based Detection of DNA."

2003 Frontiers in Chemistry – Mostafa El-Sayed Symposium, Atlanta, GA: "Light Assisted Routes to Anistropic Nanostructures."

2003 Stanford University Student Hosted Colloquium Lecturer, Palo Alto, CA: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology."

2003 DARPA Advanced Lithography Program Review – Santa Fe, NM: "Parallel, Ultrafast Sub-100 Nanometer Dip-Pen Nanolithography."

2003 CNSI Lecturer University of California, Los Angeles, CA: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology," "The Weak-Link Approach to Supramolecular Coordination Chemistry."

2003 Chemical Physics Symposium, Lecturer, University of Tel Aviv, Tel Aviv, Israel: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology."

2003 Hollingsworth Lecturer, University of Texas-Austin, Austin, TX: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology."

2003 Metzgar-Conway Fellowship Lecturer, Dickinson College, Carlisle, PA: "Nanotechnology: Small Thinking or Thing Small."

2003 University Lecturer, University of Ottawa, Ottawa, Canada: "Massively Parallel Dip-Pen Nanolithography: Toward Combinatorial Nanotechnology."

2003 Molecular Design Institute Fall Lecture, Georgia Institute for Technology, Atlanta: "Nanostructures in Biodiagnostics: Will They Make a Difference?"

2003 University of Wisconsin, Madison, WI: "Nanoparticle Probes: The Next Generation Molecular Diagnostic Indicators."

2003 226th ACS Meeting, New York, NY: "Nanoparticle Probes: The Next Generation Molecular Diagnostic Indicators," "Raman Dye-Labeled Nanoparticle Probes for DNA, RNA, and Protein Detection."

2003 Biodefense Seminar, Robert Woods Johnson Medical School, Piscataway, NJ: "Nanoparticle-Based Biodiagnostics: Towards PCR-less Detection Methods."

2003 NSF Workshop on "Nanoscience and Engineering Education" Arlington, VA: "Overview and Perspective of Nanotechnology."

2003 University of Toronto, Toronto, Canada: "Massively Parallel Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology."

2003 4th International Conference on Systems Biology, St. Louis, MO: "Ultrasensitive and Multiplexed Protein Detection with Nanoparticle-based Bio-barcodes."

2003 Symposium on Frontiers of Nanoscience and Nanotechnology, University of Michigan, Ann Arbor, MI: "Nanostructures in Biodiagnostics: Will They Make a Difference?"

2003 MRS Fall Meeting, Boston, MA: "Functional Nanostructures via Dip-Pen Nanolithography."

2003 Massachusetts Institute of Technology – Fall 2003 Nanostructures Lecture Series, Boston, MA: "Anisotropic Nanostructures: Synthetic Challenges Assembly and Biomedical Applications."

2003 Air Products Seminar, Allentown, PA: "Anisotropic Nanostructures: Synthetic Challenges, Assembly and Biomedical Applications."

2002 Keynote Speaker, Baekeland Awards Symposium and Presentation, Rutgers University, NJ: "Nanostructure-based Biodiagnostics."

2002 NSF "Small Wonders: Exploring the Vast Potential of Nanoscience", Washington, D.C. "Small is Different: From Materials to Medicine."

2002 Keynote Speaker, International Symposium on Bioanalytical Chemistry and Nanotechnology, Hunan University, China: "Nanoparticle Probes: A New Frontier in Biodetection."

2002 Gordon Research Conference, Combinatorial Chemistry, Oxford, UK: "Dip-Pen Nanolithography and Combinatorial Nanotechnology."

2002 Gordon Research Conference, Electronic Processes in Organic Mater, Salve Regina University, RI: "Dip-Pen Nanolithography and Combinatorial Nanotechnology."

2002 CNST Lecturer, University of Illinois, Urbana/Champaign, Urbana, IL: "Massively Parallel Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology."

2002 Chemistry Biology Interface Lecturer, Washington University, St. Louis, MO: "Nanoparticle-based Molecular Diagnostics: A New Frontier in Biodetection."

2002 MRS Fall Meeting, Boston, MA: "Scanning Multiplexed Raman Detection of DNA, RNA, and Protein Targets with Nanoparticle Probes," "Biodirected Synthesis of Functional Materials using Nanoscale Building Blocks."

2002 Nanoimprint and Nanoprint Technology Conference, San Francisco, CA: "Dip-Pen Nanolithography: Towards Combinatorial Nanotechnology."

2002 DOE Workshop, San Diego, CA: "Biomolecular Materials."

2002 Gordon Research Conference, Electrochemistry, Ventura, CA: "Dip-Pen Nanolithography towards Combinatorial Nanotechnology."

2002 223rd ACS National Meeting, Orlando, FL: "Three-Dimensional Assemblies Formed via the Weak-Link Approach."

2002 Gordon Research Conference, Ventura, CA: "Electrochemistry."

2002 Particles 2002, Orlando, FL: "Ultrasensitive and Selective DNA and Protein-Based Detection by Nanoparticles."

2002 Keynote Speaker, Baekeland Awards Symposium and Presentation, Rutgers University, Piscataway, NJ.

2002 NSF, Washington, D.C. "Small Wonders: Exploring the Vast Potential of Nanoscience," "Small is Different: From Materials to Medicine."

2002 DARPA/MTO Advanced Lithography Program Review, New Orleans, LA.

2002 International Symposium on Bioanalytical Chemistry and Nanotechnology, Hunan University, China: Keynote Speaker, "Nanoparticle Probes: A New Frontier in Biodetection."

2002 Gordon Research Conference: Combinatorial Chemistry, Oxford, UK: "Dip-Pen Nanolithography and Combinatorial Nanotechnology."

2002 Gordon Research Conference, Salve Regina University, Newport, R.I: "Electronic Processes in Organic Materials," "Dip-Pen Nanolithography and Combinatorial Nanotechnology."

2002 CNST Lecture, University of Illinois, Urbana/Champagne, IL: "Massively Parallel Dip Pen Nanolithography: Towards Combinatorial Nanotechnology," Urbana, IL.

2002 Progress in Biotechnology Seminar Series, UC Davis, CA: "From Nanopatterning to Nanoparticles: New Tools for Biotechnology."

2002 ACS, Boston, MA: "Template-directed Assembly of Bioinorganic Nanostructures."

2002 International Conference on Electron, Ion and Photon Beam Technology & Nanofabrication, Anaheim, CA: "Dip-Pen Nanolithography: Patterning Functional Chemical Nanostructures."

2002 MRS Spring Meeting, San Francisco, CA: "Protein and Oligonucleotide Nanoarrays Generated by Dip-Pen Nanolithography."

2001 Gordon Research Conference, Polymers West, Ventura, CA: "Dip-Pen Nanolithography."

2001 14th Biennial Marvel Symposium, University of Arizona, AZ: “Programmable Inorganic Architectures from DNA-Functionalized Building Blocks.”
2001 Pittcon, New Orleans, LA: “Redox-Active and Inactive Nanostructures Generated via Dip-Pen Nanolithography.”
2001 NSF “Partnership in Nanotechnology” Review, Arlington, VA: “DNA directed Formation of Inorganic Nanostructures.”
2001 NSF Workshop, Arlington, VA: “Non-Conventional Patterning below 50 nm.”
2001 AFOSR/ONR Electrochemistry Science & Technology Review, Annapolis, MD: “Nanostructured Materials for 3-D Structures.”
2001 University of Rochester, Rochester, NY: “Programming the Formation of 2- and 3-Dimensional Inorganic Architectures with DNA.”
2001 Electrochemical Society Meeting, Washington, DC: “Scanometric DNA Array Detection with Nanoparticle Probes.”
2001 ACS, Symposium on Macromolecular Self-Assembly and Surfaces and Interfaces, San Diego, CA: “Dip-Pen Nanolithography: A New Tool for Studying Template-Driven Particle Assembly and Crystallization.”
2001 75th ACS Colloid and Surface Science Symposium, Pittsburgh, PA: “Dip-Pen Nanolithography: A Tool for Generating Organic and Biological Surface Architectures witch 5 nm Resolution.”
2001 DARPA Review, Duck Key, FL: “Dip-Pen Nanolithography State-of-the-Art Applications and Future Challenges.”
2001 Gordon Research Conference, Chemical Sensors & Interfacial Design, Lucca, Italy: “Nanoparticle-based Probes: New Opportunities in DNA Diagnostics, Gene-Expression, and arrays.”
2001 MRS, San Francisco, CA: “Terthienyl and Polyterthienyl Ligands as Redox Switchable Hemilabile Ligands for Oxidation-State Dependent Molecular Uptake and Release,” “Two- and Three-Dimensional DNA-driven Assembly of Colloidal Materials,” “Core-Shell Nanoparticles Formed from Ring- Opening Metathesis Polymerization and Functional Biomolecules,” “Dip-Pen Nanolithography and Combinatorial Nanotechnology.”
2001 CSC Conference, Montreal, Canada: “Ultrasensitive and Selective Biomolecule-Detection Based upon Nanoparticle Materials.”
2001 ACS Colloid and Surface Science Symposium, University of Pittsburgh, PA: “Dip-Pen Nanolithography: A Tool for Generating Organic and Biological Surface Architectures with a 5nm resolution.”
2001 Gordon Research Conference, Organic Thin Films, Salve Regina, Newport, R.I: “Bio-Inspired Materials from Inorganic Nanoparticles and DNA.”
2001 Gordon Research Conference, Polymers (East), New Hampshire: "2- and 3-D Nanoparticle Arrays.”
2001 Gordon Conference in Analytical Chemistry, New London, CT: “Functional Materials from DNA-Modified Nanostructures.”
2001 American Chemical Society, National Meeting, Chicago, IL: “Metals in Medicine.”
2001 Carnegie Mellon University, Pittsburgh, PA: “Dip-Pen Nanolithography.”
2001 Kilpatrick Symposium on Nanotechnology, Chicago, IL: “Dip-Pen Nanolithography: A Route towards Combinatorial Nanotechnology.”

2001 Chicago Technology Forum, Chicago, IL: "Platform Technologies/New Companies Nanotechnology and DNA Assays."
2001 American Association for Clinical Chemistry, San Diego, CA: "New Biological Diagnostic Tools through Nanotechnology."

Ratner

2005 University of Colorado, Denver, CO: "Theoretical Studies of Self-Assembly of Peptide Amphiphile Nanostructures."
2005 Bio-inspired Nanoscience and Molecular Machines Conference PASI–NSF, Bariloche, Argentina: "Studies in Self-assembly of Supramolecular Nanostructures (Poster)
2005 229th ACS National Meeting, San Diego, CA: "Studies in Self-Assembly of Supramolecular Nanostructures."
2004 Kodak Research Labs, Rochester, NY: Williams Lecturer.
2004 Argonne National Laboratory, Argonne, IL: Invited talk on Nanoscience.
2004 Director's Lecturer, NIST, Gaithersburg: Koshland Lecturer, Haverford College.
2004 Michl Lecturer, University of Colorado.
2004 University of Missouri-Rolla, Rolla, MO: "Theoretical Studies of Self-Assembly of Peptide Amphiphile Nanostructures."
2004 227th ACS National Meeting, Anaheim, CA: "On the Structure and Stability of Self-Assembled Zwitterionic Peptide Amphiphiles."
2004 36th Midwest Theoretical Chemistry Conference, Michigan State University, East Lansing, MI: "All-Atom Numerical Studies of Self-Assembly of Zwitterionic Peptide Amphiphiles."
2004 University of California, Los Angeles, CA: CMI Lecturer.
2004 University of Texas, Austin, TX: Matsen Lecturer.
2004 Queen's University, Kingston, Ontario, Canada: Frost Lecturer.
2003 Florida State University, Tallahassee, FL: "Theoretical Studies and Modeling of Peptide-Amphiphiles' Self-Assembly."
2003 University of South Florida, Tampa, FL: "Theoretical Studies and Modeling of Peptide Amphiphiles' Self-Assembly."
2003 Duquesne University, Pittsburgh, PA: "Assembly Methods for Molecular Scale Structures."
2003 225th ACS National Meeting, New Orleans, LA: "Theoretical Studies and Modeling of Peptide Amphiphile Nanostructures."
2003 Northwestern University Symposium on Materials, Northwestern University, Evanston, IL: "Nanostructured Surface Assemblies."
2003 University of Pittsburgh, Pittsburgh, PA: "Theoretical Studies and Modeling of Peptide Amphiphile Nanostructures."
2003 35th Midwest Theoretical Chemistry Conference, Iowa State University, Ames, IA: "Theoretical Studies of the Self-assembly of Peptide Amphiphile Nanostructures."
2003 Invited Talk, University of Nevada at Reno, Reno, NV: "Theoretical Studies of the Self-Assembly of Peptide Amphiphile Nanostructures."
2003 Invited Talk, Wayne State University, Detroit, MI: "Theoretical Studies of the Self-Assembly of Peptide Amphiphile Nanostructures."

2002 Foresight Institute Meeting, Washington, D.C.: "Assembly in Transport and Molecular Junctions."
2002 MDC Lectures, Georgia Institute of Technology, Atlanta, GA: "Nanoscale Assembly and its Molecular Mechanisms."
2002 Inter-American Statistical Mechanics Program Workshop, University of New Mexico, Albuquerque, NM: "Nanoscale Assembly and Molecular Interactions: Artificial Bone Structures."

Schatz

2005 DARPA Workshop on SERS, San Francisco, CA: "Electronic Structure Studies and Mixed QM/ED Studies of SERS."
2005 American Conference on Theoretical Chemistry, UCLA, Session Chair on Biophysics Theory.
2005 IAMS Retreat, Taipei, Taiwan: "Reactive Collision Dynamics: Metal Nanoparticle Optical Properties."
2005 NSF Summer Institute on Nanomechanics and Materials, Northwestern University, Evanston, IL: "Empirical Potential Modeling of Proteins; Computational Chemistry; Modeling Bioadhesion."
2005 SPP2 Conference, Graz, Austria: "Theoretical Studies of Nanoparticle and Nanohole Arrays."
2005 Foundations of Nanoscience, Session Organizer, Track on DNA/Nanoparticle Aggregates, Snowbird, UT.
2005 ACS national Meeting, San Diego, CA: Biological Sensing with Silver Nanoparticles and Nanoparticle Arrays: Theoretical Studies: The Pople Years at Northwestern: A Dynamicist Learns Electronic Structure Theory," New Uses for Electronic Structure and Molecular Dynamics Calculations."
2005 University of Chicago, Chicago, IL: "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory."
2005 University of Michigan, Ann Arbor, MI: "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory."
2005 University of Buffalo, Buffalo, NY: "Nanoparticle Optical Properties and Biomolecule Detection: New Challenges for Theory."
2005 Skokie, IL: "DNA Melting and Optical Sensors."
2004 Queen's University, Kingston, ON, Canada: "Nanoparticles and Biomolecule Detection: New Challenges for Theory."
2004 DuPont, Wilmington, DE, Seminar: "Metal Nanoparticle Optical Properties and DNA Structures and Thermodynamics."
2004 Pusan National University, Busan, Korea: "Nanoparticles and Nanoconfined DNA: New Challenges for Theory."
2004 Particles Meeting, Orlando, FL: "Optical Properties of Anisotropic Particles".
2004 ACS National Meeting, Anaheim, CA: "Anisotropic Metal Properties," "DNA Melting and Dynamics," "Optical Properties of Arrays of Nanoparticles," "Self-Assembly Processes in Peptide Amphiphiles."
2004 Conference on Theoretical and Computational Chemistry, Giongiu, Korea: "Carbon Nanotube Fracture and Hypothermal Chemistry."

2004 Foundations of Nanoscience Meeting, Snowbird, UT: "DNA Structural and Thermal Properties."
2004 University of Pisa, Pisa, Italy: "Nanoparticle Optical Properties and DNA Detection: Theoretical Studies."
2004 University of Siena, Siena, Italy: "Theoretical Studies of DNA Structures and Dynamics."
2004 University of Colorado, Bolder, CO: "Nanoparticles and Nanoconfined DNA: New Challenges for Theory."
2003 Gordon Conference on Electronic Spectroscopy and Dynamics, Bates College, ME: "Optical Properties of Metal Nanoparticles and Nanoparticle Arrays."
2003 Argonne National Laboratory, Center for Nanomaterials, Argonne, IL: "Nanoparticle Optics and DNA Melting."
2003 Beckman Institute, University of Illinois at Urbana-Champaign, IL: "Modeling Dynamical Processes in Materials."
2003 Stanford University, Stanford, CA: "Nanoparticles and Nanoconfined DNA: New Challenges for Theory."
2003 Morrison Inaugural Lecture, Northwestern University, Evanston, IL: "Theory and Nanoparticles."
2003 Michigan State University, East Lansing, MI: "Theoretical Studies of Nanoparticles and DNA."
2003 Northwestern Chemistry Department Industrial Affiliates, Evanston, IL: "Nanoparticle Optical Properties and DNA Sensing."
2003 Tutorial on Nanoparticle Optical Properties, Summer Nanoschool at Argonne National Laboratory.
2002 Montana State University, Bozeman, MT: "Theoretical Studies of Nanoparticles and DNA."
2002 Workshop Illinois Benedictine University: "Nanoparticle Optical Properties and DNA Sensing."
2002 PASI, Joint Argentina-NSF Workshop on Ferroelectrics, Rosario, Argentina: "Nanopatterning of Addressable Functional Inorganic Nanostructures."
2002 MRS Annual Meeting, Boston MA: "Structural, Thermodynamic and Optical Properties of DNA-linked Metal Nanoparticle Aggregates and Arrays: Theoretical Studies."
2002 Workshop in Information and Communication at the National Academy of Sciences: "Chemical Sciences in the 21st Century Initiative of the NAS."
2001 CCTCC (Current Trends in Computational Chemistry) Meeting, Jackson, MS: "Dip-Pen Nanolithography."

Stupp

2005 Royal Society of Chemistry, 7th International Conference on Materials Chemistry, Plenary Lecture, Edinburgh, Scotland: "Self-Assembly Codes for Organic Materials."
2005 USA-Japan Forum, Advances in Polymer Chemistry and Their Impacts Upon Society, South Lake Tahoe, CA: "Self-Assembly of Polymeric Objects: Form and Function."

2005 Polymers (East) Gordon Research Conference, South Hadley, MA: "Control of Nanoscale Chirality and Cell Recognition in Bio-inspired Polymers."

2005 Sir Edward Youde Memorial Fund Visiting Professorship, Hong Kong University of Science and Technology, Hong Kong: "Biomolecular Nanostructures" and "Nanotechnology for Regenerative Medicine."

2005 Procter and Gamble Lecture Series hosted by the Hispanic Organization for Multidisciplinary Interaction in Education and Science, University of California, Los Angeles, CA: "Form and Function of Supramolecular Nanostructures."

2005 Association for Research in Vision and Ophthalmology (ARVO), Nanotechnology and Medicine, Applications for Vision Research, Ft. Lauderdale, FL: "Nanotechnology and Regenerative Medicine."

2005 Georgetown University, Departments of Chemistry, Biology, and Physics, Spring Seminar, Washington, D.C.: "Form and Function of Supramolecular Nanostructures."

2005 NSF Distinguished Lecturer in Mathematical and Physical Sciences, Washington, D.C.: "Biomaterials for Human Repair."

2005 7th International Symposium on the Composition, Properties and Fundamental Structure of Tooth Enamel, Enamel VII, Brewster, MA: "Self-Assembly and Biomimetic Mineralization."

2005 University of Utah, Department of Chemistry, Salt Lake City, UT: "Self-assembly of Supramolecular Nanostructures."

2005 ACS National Meeting, San Diego, CA: "Self-Assembly of Polymeric Objects: Form and Function."

2005 Cancer and Nanotechnology Symposium, Plenary Lecture, Georgetown University: "Bioactive Nanostructures as Protein Mimics."

2005 AAAS Annual Meeting, Washington, D.C., Symposium on Nanotechnology, Bio-inspired Materials and Nanosystems: "Bioactive Nanostructures."

2005 Gordon Research Conference, Polymers (West), Ventura, CA: "Cellular Interactions with Polymeric Surfaces."

2005 Biomolecular and Biomimetics Self-Assembly Workshop, Merida, Mexico: "Bioactive Nanostructures as Protein Mimics."

2004 Materials Research Society Fall Meeting, Boston, MA: "Hybrid Materials and Self-Assembling Phases," "Micron and Nanoscale Materials Interfaced with Biology and Medicine."

2004 Stein-Bayer Seminar Lecturer, University of Massachusetts, Amherst, MA: "Crafting Supramolecular Polymers for Bioactivity."

2004 Alan Lawley Lecture Series in Materials, Drexel University, Philadelphia, PA: "Self-Assembly of Supramolecular Nanostructures."

2004 Industrial Physics Forum, Corporate Associates Advisory Committee, IBM Watson Research Center, Yorktown Heights, NY: "The Interface of Nanotechnology with Supramolecular Chemistry and Biology."

2004 Society for Biomaterials, Biomaterials in Regenerative Medicine: The Advent of Combination Products, Philadelphia, PA: "Crafting Nanoscale Bioactivity in Biomaterials with Supramolecular Chemistry."

2004 Gordon Research Conference, Drug Carriers in Medicine and Biology, Big Sky Resort, MT: "Self-Assembling Materials for Regeneration of Human Tissue."

2004 Frontiers Symposium, Lawrence Livermore National Laboratory, Livermore, CA: "Pushing the Self-Assembly Envelope to Create Biomimetic Materials and Functions."

2005 PASI-NSF: Bio-inspired Nanoscience and Molecular Machines, Bariloche, Argentina: "Biomimetic Self-Assembly of Nanostructures," and "Bionanotechnology for Regenerative Medicine."

2004 MRS Fall Meeting, Boston, Massachusetts: "Hybrid Materials and Self-Assembling Phases," and "Micron and Nanoscale Materials Interfaced with Biology and Medicine."

2004 Wulff Lecture, Massachusetts Institute of Technology, Boston, MA: "Materials Science for the Repair of Humans."

2004 International Symposium BMMP-4, Nagoya University, Nagoya, Japan: "Mineralization of Biomimetic Nanofibers with Semiconductors, Magnets, and Bone Crystals."

2004 3rd International 21st Century Center of Excellence Symposium, Osaka University, Osaka, Japan: "Pushing the Self-Assembly Envelope to Mimic Biology's Materials and Functions."

2004 US-Japan Seminar Workshop on Directed Self-Assembly and Self-Organization, University of California, Santa Barbara, CA: "Self-Assembly of Bioactive Nanostructures."

2004 Procter & Gamble Polymer Science Symposium: "The New Organic Materials for Technology."

2004 I.S.I.S University Louis Pasteur, Strasbourg, France: "Self-Assembly of Supramolecular Materials," "Supramolecular Crafting of Bioactivity", and "Self-Assembly of Supramolecular Materials."

2004 Frontiers in Polymer Technology, San Ramon, CA: "Self-Assembling and Biomimetic Materials."

2004 Argonne Center for Nanoscale Materials, First User Meeting, Argonne, IL: "Nanoscience in Advanced Medicine."

2004 MRS Spring Meeting, San Francisco, CA: "Biological and Bio-Inspired Materials and Devices," "Hybrid Biological-Inorganic Interfaces."

2004 ACS Annual Meeting, Anaheim, CA: "Luminescent and Mineralized Liquid Crystals."

2004 NSF Garcia MRSEC, CNRS, Institute Curie, Physics and Biology: A Materials Approach, Paris, France: "Biomolecular Self-Assembly."

2004 Laboratory for Memory and Learning, Brain Science Institute, RIKEN, Saitama, Japan: "Self-Assembly of Regenerative Matrices for Neurons."

2004 Unilever R&D Colworth, Sharnbrook, Bedforshire, UK: "Emerging Opportunities in Soft Nanotechnology and Self-Assembly."

2004 Gordon Research Conference on Signal Transduction by Engineered Extracellular Matrices, Bates College, Lewiston, ME: "Supramolecular Signaling by Self-Assembling Extracellular Matrices."

2003 AFOSR Program Review - Biometric, Biomaterial, and Bio-interfacial Sciences Program, Hawk's Cay, FL: "Ultra-Sensitive and Selective Chip-Based Detection of DNA," "Surface Templated, Bio-Inspired Synthesis and Fabrication of Functional Materials."

2003 PittCon Conference, Orlando, FL: "Building a High-Tech Company in a University Environment," "Novel Nanoparticle-Based Approaches to High Sensitivity Biomolecule Detection."
2003 ACS National Meeting, New Orleans, LA: "Nanoparticle-Oligonucleotide conjugates: A New Frontier in Biodiagnostics."
2003 Inauguration of Bioengineering Institute, Barcelona, Spain: "Bioengineering in the Nanotechnology Era."
2003 MRS Fall Meeting, Boston, MA: "Pushing the Self-Assembly Envelope to Mimic Biology's Materials and Functions."
2003 Northwestern University, Seminar, Department of Bioengineering, Evanston, IL: "Self-Assembling Scaffolds for Regenerative Medicine."
2003 NATO-Advanced Study Institute (ASI) on "Learning from Nature How to Design New Implantable Biomaterials: From Bio-mineralization Fundamentals to Biomimetic Materials and Processing Routes," Opening Lecture, Alvor, Algarve, Portugal: "Mineralization of Organic Templates: Mechanisms and Order in Bio-mineralization."
2003 DSM, Holland: "The New Organic Materials for Technology."
2003 International Dendrimer Symposium (IDS-3), Berlin, Germany: "Self-Assembly of Dendritic Molecules and its Impact on Materials."
2003 Gordon Research Conference, Chemistry of Supramolecules and Assemblies, Proctor Academy, Andover, MA.
2003 Polynanomeres: A Matrix for Design to Build Processes, Porto Heli, Greece.
2003 Gordon Research Conference, Polymers (East), Mount Holyoke College, South Hadley, MA.
2003 NanoBio Forum, San Francisco, CA.
2003 Nanoscience & Technology Conference, Gronigen, Netherlands.
2003 Energy & Nanotechnology: Strategies for the Future, Rice University, Houston, TX.
2003 Nanoarchitectonics Workshop: "Nanospace Engineering for Nanoarchitectonics," Tsukuba, Japan.
2003 225th ACS National Meeting, Plenary Lecture, New Orleans, LA.
2003 University of Oxford, Oxford, UK.
2003 International Symposium BMMP-3, Nagoya, Japan.
2002 Paris Sciences, Paris, France.
2002 Unilever Nanotechnology Spark Workshop, London, UK.
2002 US-Japan Polymer Seminar "Advanced Polymer Chemistry for the 21st Century", Nagoya, Japan.
2002 Polymers in Medicine and Biology Workshop, Sonoma Valley, CA.
2002 6th New Jersey Symposium on Biomaterials Science, Somerset, NJ.
2002 Debye Institute, Utrecht University, Netherlands.
2002 XIIth International Symposium on Supramolecular Chemistry, Plenary Lecturer, Eilat, Israel.
2002 17th European Conference on Biomaterials, Barcelona, Spain.
2002 Nanoscale Science and Technology Forum 2002, Max Planck Institute, Mainz, Germany.
2002 ACS, Fall Meeting, Boston, MA.

2002 International Workshop on Ceramic and Metal Interfaces Control at the Atomic Level, Oviedo, Spain.
2002 Gordon Research Conference on Bioorganic Chemistry, Andover, NH.
2002 Institute for Materials Research and Engineering, Singapore.
2002 Chemistry Colloquium, Carnegie Mellon University, Pittsburgh, PA.
2002 Necker Lecture, Southern Illinois University, Carbondale, IL.
2002 ACS, Spring Meeting, Orlando, FL.
2002 MRS, Spring Meeting, San Francisco, CA.
2002 Baekeland Award Symposium, Rutgers University, NJ.
2002 National Science Foundation, Small Wonders Workshop.
2002 Polymer Science Colloquium, University of Akron, OH.
2002 Chemistry Colloquium, Columbia University, New York, NY.
2002 29th Rauscher Lecture, Rensselaer Polytechnic Institute, Troy, NY.
2001 MRS Fall Meeting Boston, MA.

Chandrasekhar
2003 ASME Nanotechnology BootCamp, Northwestern University.

Ghadiri
2001 DOE workshop, San Diego, CA.

B. Consultative/Advisory Functions

Dravid
Dravid is a member of the Scientific Advisory Boards of NanoInk Inc., Chicago, IL. (2003-2004) and Kalinex, Inc., Berkeley, CA (2003-2004). In the past he has also been a member of the Program Review Committee, Materials Science Division, Lawrence Berkeley National Laboratory (LBNL) and Department of Energy, BES. He also serves as a consultant/advisor on TEM analysis of high-performance structural alloys for the Department of the Navy.

Kaplan
Kaplan has been a member of the AFRL/ML Scientific Advisory Board Member (2003-2004). He also was an external Reviewer for the US ARO Life Sciences Program (2003-2004).

Mirkin
Mirkin consults for NanoInk, Nanosphere, Kirkland & Ellis LLP, and NextGen Aeronautics. He is also a member of NanoInk's and Nanosphere's Scientific Advisory Boards (2002-present). In the past he has consulted for Monsato Company, Physical Optics Corporation, Dow Chemical Corporation, Calmec Corporation, Hexagon Packaging, and Pharmacia.

Ratner
Ratner is the Chair of the Technical Advisory Board on Materials at the Dow Chemical Company. He has also been working closely with Clive Bosnyak and his colleagues at the Dow Chemical Company on the topic of smart surfaces. In addition, he has

collaborated with Drs. Shashidhar (NRL) and Karna (ARL) on transport through metallic lines as assembled by DPN methods and molecular electronics, respectively, and with David Rauh and colleagues at EIC Laboratories in Norwood, MA on studies of the alignment and structural assurance in extended phthalocyanine materials.

Schatz
Schatz was a member of an SBIR NSF review panel on Biotechnology March 24-26, 2003. He also collaborated with Paul Sheehan, Lloyd Whitman and Rich Colton of the Naval Research Laboratory (NRL) on the theory of DPN (2001-2004), and he consulted for DuPont on chemical and biological detection based on nanoscale materials (2003-2004).

Stupp
Stupp is a founding Member of the Scientific Advisory Committee, Center for Nanoscale Materials, Argonne National Laboratory (2003-present), and a Co-founder and Chief Scientific Officer of NanoMateria, Inc (2002-present). He is also a member of the Scientific Advisory Board of the National University of Singapore, Graduate School for Integrative Sciences & Engineering (2003-present), of the External Advisory Board of the Materials Research Science and Engineering Center (MRSEC) on Nanostructured Materials and Interfaces at the University of Wisconsin-Madison (2002-present), a member of the Solid State Sciences Committee of the National Academy of Sciences (2001-present), of the Review Board of Canadian Arthritis Foundation (2000-present), and of the Scientific Advisory Board at Baxter (2001-present). In the past he was co-chair of the DOE workshop "Biomolecular Materials", La Jolla, CA (2002), he participated in a U.S. Senate Roundtable Discussion on Nanotechnology&Medicine, Senate Committee on Health, Education, Labor and Pensions (2003), in a NSF/NIH Workshop on Nanobiotechnology, Washington, DC, (2003). He was also a senior member of the Selection Committee of the Institute Universitaire de France (2003), and of the Nanotechnology Technical Advisory Group (TAG) of the President's Council of Advisors on Science and Technology (PCAST) (2003-2004).

Chandrasekhar
Chandrasekhar was a member of the NSF Proposal and SBIR Review Panels, October 2002 and April 2003.

C. Transitions

Dravid
Dravid collaborated with Drs. Steve Semincik (NIST) and Thomas Thundat (oak Ridge National Laboratory) on the use of microheaters in combination with DPN nanopatterning of semiconducting oxide sensors for toxic gas and detection of biological warfare agents (BWA). He also collaborated with Dr. Frank Schweighardt at Air Products on boundary conditions and practical considerations for in-process gas sensor requirements, and with researchers at NanoInk Inc. on the development of a positioning device for scanning probe microscopy (SPM) for site-specific specimen registration.

Kaplan
Technology from Kaplan's research related to the self-assembly of peptides and proteins into liquid crystalline phase was transitioned to the start-up company Evolved Nanosciences, Inc. (ENS).

Mirkin
Mirkin has collaborated with Dr. Ratna Shashidhar (NRL) on templating biological and nanoparticle-based architectures using DPN functionalization of surfaces. This collaboration led to a joint grant proposal entitled "DPN Patterning of a Single Virus and Nanoparticles for Molecular Electronics," which was funded by the Office of Naval Research (2003-2004). He has also collaborated with research personnel at NRL and Wright Patterson AFB to transition DPN and to develop a sound understanding of the various transport mechanisms, and with Dr. Tim Gierke at DuPont on the fundamentals of mesoscopic materials. DPN technology was licensed to NanoInk, Inc and DPN software commercialized and distributed to academic, DoD and industrial labs.

Ratner
Ratner collaborated with Dr. David Rauh, of EIC Laboratories on nanoscale assembly application methods, and with Dr. Clyde Bosynak of Dow Chemical Company on the preparation of smart structures, using a variety of methods including DPN.

Schatz
Schatz worked with Issi Dunietz at Integrated DNA Technologies (IDT) and Stephen Gray at Argonne National Laboratory on models of DNA melting and the theory of electromagnetic light scattering methods and software, respectively. He also collaborated with Lloyd Whitman (NRL) on modeling of the structure of single-stranded DNA on gold surfaces, and with James Prober at Dupont on SERS theory and protein detection.

Stupp
Northwestern University licensed technology originating from Stupp's research to the start-up company NanoMateria, Inc. The company intends to commercialize self-assembling and mineral templating technology.

5. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

A. New Discoveries

Mirkin

1. Developed electrochemically whittling to reduce the size of DPN generated alkanethiol nanostructures on gold surfaces.
2. Developed a protocol to fabricate metal-organic based biomolecule nanoarrays, e.g. single virus and antibody nanoarrays/
3. Template-based electrochemical fabrication and assembly of metal-polymer composite nanorods into 3-D superstructures.
4. Development of a highly selective and sensitive coordination chemistry and DPN-based immuno-assay.
5. Developed a strategy to fabricate solid-state structures and nanowells on surfaces in a massively parallel fashion.

6. Synthesis of DNA-polymer amphiphiles with recognition properties that assemble into spherical micelle structures.
7. Development of a high-throughput DPN-based technology to generate high-density nanoarrays of biological supramolecular structures, and high-throughput, high-resolution lithography method, called "on-wire lithography" (OWL) for lithographic processing of one-dimensional dented, metallic nanowires.

Ginger

1. Nanoscale DPN templates as a guide to direct nucleation, growth, and pattern formation of different polymer phases during spinodal decomposition.

Ratner

1. Developed pH/salinity diagrams for PA molecules.
2. Self-assembly of Mesoscopic Au/PPy amphiphiles.

Schatz

1. Developed models for surface diffusion in SAMs composed of alkylthiols.
2. Surface adhesion modeling

Dravid

1. Developed high sensitivity miniature DPN-derived chemical nanosensors.
2. Direct nanopatterning of conducting polymers using precursor inks (e.g., polypyrrole) in-between patterned electrodes for potential sensing/detection applications.
3. Development of a new method for fast and convenient sample repositioning for atomic force microscopy related to lithographic and imaging techniques.
4. Patterning of 3-D nanostructures using soft lithography. A Northwestern University Invention Disclosure was filed in July 2005.
5. Fabrication of high sensitivity miniature DPN-derived chemical nanosensors using Pt-doped SnO_2.
6. In-house fabrication of an integrated prototype for gas sensing using DPN-derived sensor elements.

Kaplan

1. Smectic phase formation from collagens via self-assembly.
2. Formation of conducting polymers on surfaces using DPN and biocatalytic reactions at ambient conditions.
3. Surface-induced regioselective enzymatic polymerization of caffeic acid on DPN patterns.

Ghadiri

1. Designed and synthesized conductor and semi-conductor self-assembled cyclic D,L-α peptide nanotubes.
2. Developed a method to synthesize cyclic peptides bearing 1,4,5,8-naphthalenetetracarboxilix diimide (NDI) to modify the electronic structure of the peptide.

Stupp

1. Self assembly of peptide amphiphile (PA) nanofibers and peptide lipid (PL) hybrid molecules.
2. Grafting and large parallel arrays of Nanofibers by self assembly on titanium dioxide surfaces.
3. Developed a protocol for supramolecular PA patterning using diaminopyridine alkanethiol (DAP) as ink.

B. New Inventions and/or Patent Disclosures

Dravid

1. Dravid, V.P. "Nanopatterning of Solid-State Structures via Dip-Pen Nanolithography" 2001.
2. Dravid, V.P. "Nanopatterning of "Hard" Magnetic Nanostructures via Dip-Pen Nanolithography and a Sol-Gel Process" 2002.
3. Dravid, V.P. "Multifunctional Nanosensors for bio-, chemical and gaseous sensing and diagnostics" 2002.
4. Dravid et al. "Multifunctional Nanosensors for bio-, chemical and gaseous sensing and diagnostics" NU disclosure.
5. Dravid et al. "Patterning Solid State Features Via Dip Pen Nanolithography with Sol-Based Inks" US Provisional Application #60/341,614.
6. Dravid et al. "Nanopatterning of 'Hard' Magnetic Nanostructures Via Dip-Pen Nanolithography and a Sol-Based Ink" US Patent Application # 60/410,952.
7. Dravid et al. "DPN printing with open tips; aperture pen nanolithography NU 21009, "#083847-0208 Patent Application # 10-059,593.
8. Dravid, V. et al "A Convenient and Rapid Sample Repositioning System for Atomic Force Microscope" (Invention disclosure: NU 23120).
9. Dravid, V. et al. "Individually addressed large scale patterning of conducting polymers by localized electric fields" (Invention disclosure: NU 23097).

Kaplan

1. Valluzzi, R.; Kaplan, D.L.; "Self-Fabricating Materials Based on Collagens" Patent Disclosure.
2. Volloch, V.; Kaplan, D.L. "Control of Cellular Aging by Fibrous Protein Structure".
3. Kaplan, D.L.; Xu, P.; Wilson, D.; Singh, A. "Wiring Cells: 'Drawing' Connectors Between Cells and Microchips/MEMS Biocatalytic Processes for Surface Patterning Using DPN".

Mirkin

1. Mirkin, C.A.; Lim, J-H. "Electrostatically Driven Dip-Pen Nanolithography of Conducting Polymers" Prov. # 60/382,596.
2. Mirkin, C.A.; Garimella, V. "Method for Immobilizing Molecules onto Surfaces" International Patent Application No. PCT/US02/22128.
3. Mirkin, C.A.; Dravid, V.; Su, M. 'Patterning Solid-State Features via Dip-Pen Nanolithography with Sol-based Inks" US Application 10/320,721.

4. Mirkin, C.A.; Demers, L.; Ginger, D. “Direct-Write Nanolithographic Deposition of Nucleic Acids from Nanoscopic Tips” Formal Application 10/307,515.
5. Fu, L.; Liu, X.; Dravid, V.; Mirkin, C.A. “Nanopatterning of ‘Hard’ Magnetic Nanostructures Via Dip-Pen Nanolithography and a Sol-Based Ink” US Application 60/410,952.
6. Mirkin, C.A.; Zhang, H.; Chung, S.W. “Fabrication of sub-50nm Solid State Nanostructures Based on Dip-Pen Nanolithography” US Application 10/725,939.
7. Mirkin, C.A.; Zhang, H.; Lee, K.-B.; Li, Z. “Biofunctionalized Nanoarrays of Inorganic Structures Prepared by Dip-Pen Nanolithography” (NU 23023)
8. Mirkin, C.A.; Zhang, H.; Liu, C. “Scanning Probe Contact Printing” US Application 10/671,381.
9. Mirkin, C.A.; Lim, J.-H.; Ginger, D.; Lee, K.-B.; Nam, J.-M.; Demers, L. “Peptide and Protein Nanoarrays and Direct-Write Nanolithographic Printing of Peptides and Proteins” US Application 10/788,414.
10. Mirkin, C.A.; Liu, X.; Guo, S. “Surface- and Site-specific Ring-Opening Metathesis Polymerization Initiated via Dip-Pen Nanolithography” US Application 60/488,094.
11. Mirkin, C.A.; Zhang, H. “Fabrication of Solid-State Nanostructures Using Resist-Layers Generated by Dip-Pen Nanolithography” (NU 23101).
12. Mirkin, C.A.; Park, S.; Lim, J.-H.; Chung, S.-W. ”Self-Organizatiom of Metal Conducting Polymer Composite Nanowires into 3-Dimensional Tubular Suprastructures” Provisional Patent Application 60/500,056.
13. Mirkin, C.A.; Lee, K.-B.; Park, S. “Multi-Component Magnetic Nanorods for Biomolecular Separation” US Provisional Application 60/530,797.
14. Mirkin, C.; Zhang, H.; Jin, R. “Synthesis of Open-Ended, Cylindrical Au-Ag Alloy Nanostructures on a Si/SiOx Surface” (NU 24028).
15. Mirkin, C.A.; Gianneschi, N. “Allosterically Catalyzed Signal Amplification” (NU 24081).
16. Mirkin, C.A.; Qin, L.; Park, S.; Huang, L. “On-Wire Lithography: high Throughput Nanogaps and Nanorod/Disk Arrays” US Provisional Patent Application 60/661,659.
17. Mirkin, C.A.; Rozhok, S. “A Compact Precision XY Microposition for the Optical Microscope System of Commercial DPN Writes with AFM (NScriptor) to Locate and Monitor One- or Two-Dimensional Multiple-Probe Array over the Sample Surface” (NU 25041).
18. Mirkin, C.A.; Oh, M. “Chemically Tailorable Nanoparticles Realized Through Metal-Metallo Ligand Coordination Chemistry” US Provisional Application 60/685,786.
19. Mirkin, C.A.; Comamala Maspoch, D.; Shen, C.K.-F.; Kakkassery, J.; Vega, R. “Coordination Chemistry Based Immobilization of Unmodified Proteins, Viruses, and Cells” (NU 25045).
20. Mirkin, C.A.; Salaita, K. “Phase separation Induced Miniaturization of Patterned Structures” US Provisional Application 60/697,053.
21. Mirkin, C.A.; Vega, R.; Comamala-Maspoch, D.; Salaita, K. “Generating Nanoarrays of Single Virus Particles by Dip-Pen Nanolithography” US Provisional Application 60/712,432.

22. Mirkin, C.A; Wang, Y.; Comamala-Maspoch, D. “Solution-based Assembly of Carbon Nanotubes and other Nanoscale Building Blocks” US Provisional Patent Application 60/741,837.

Stupp

1. Stupp, S. I. “Self-Assembly and Mineralization of Peptide-Amphiphile Nanofibers” U.S. Provisional Application Serial No. 60/333,074.
2. Stupp, S. I. “Peptide-Amphiphile Solutions and Self-Assembled Peptide Nanofiber” Networks U.S. Provisional Application Serial No. 60/369,638.
3. Stupp, S. I. “Charged Peptide Amphiphile Solutions and Self-Assembled Peptide Nanofiber” Networks formed there from U.S. Provisional Application.
4. Stupp et al. Self-Assembled Peptide Amphiphiles & Self-Assembled Peptide Nanofiber Networks Presenting Multiple Signals: U.S. Provisional Serial No. 60/413,101.
5. Stupp et al. Composition and Method for Simultaneous Self Assembly and Mineralization of Peptide Amphiphiles: U.S. Provisional Serial No. 60/245,689.
6. Stupp et al. Self Assembly of Multi-Dimensional Peptide Amphiphiles: U.S. Provisional Serial No. 60/245,536.
7. Stupp, S.I. et al. “Compositions and Method of Making Branched Peptide Amphiphiles and Self Assembled Structures Therefrom” Provisional Application.

5. Honors and Awards

Dravid

2005 American Ceramic Society Ceramographic Awards (Donthu/Dravid)
2004 Elected Fellow of the American Ceramic Society
2004 Editor: Microscopy and Microanalysis, Journal of Microscopy Society of America
2003 American Ceramic Society Ceramographic Awards, Nashville, TN (Dravid/Su)
2003 Presidential Graduate Student Award, Microbeam Analysis Society (MAS), San Antonio, TX (Dravid/Su)
2002 American Ceramic Society 1st Place (Dravid, Mirkin)
2001 Visiting Faculty Fellow: ASM-IIM Faculty Fellowship
2001 MSE Department: Teacher of the Year Award 2001-2002
2001 Distinguished Alumnus Award: IIT Bombay, India

Ghadiri

2001 Elected Fellow, American Association for the Advancement of Science

Kaplan

2003 Elected Fellow to the American Institute for Medical and Biological Engineering

Mirkin

2004 NIH Director’s Pioneer Award
2004 Collegiate Inventors Award, National Inventors Hall of Fame
2004 Pennsylvania State University Outstanding Science Alumni Award
2004 Dickinson College Honorary Degree
2003 Collegiate Inventors Award, National Inventors Hall of Fame

2003 Raymond and Beverly Sackler Prize in the Physical Sciences
2003 Dickinson College Metzger-Conway Fellowship Award
2003 ACS Nobel Laureate Signature Award for Graduate Education in Chemistry
2002 Feynman Prize in Nanotechnology (NU)
2002 Ceramographic Competition, American Ceramic Society 1st Place Entry
2001 Leo Hendrick Baekeland Award

Ratner
2005 Honorary D.Sc. from the Hebrew University of Jerusalem (Ratner)
2005 Mulliken Medal from the University of Chicago (Ratner)
2004 Elected to the Royal Danish Academy of Science (Ratner)
2004 Elected to The National Academy of Science
2004 Elected to The International Academy of Quantum Molecular Sciences
2004 Elected Foreign Member of Royal Danish Academy of Sciences Society
2003 Elected to the International Academy of Quantum Molecular Sciences
2003 Elected Chair, Division of Chemical Physics of the American Physical Society
2003 Appointed Chair of the 2008 American Conference on Theoretical Chemistry
2002 Membership in the National Academy of Sciences
2001 Member, American Academy of Arts and Sciences
2001 Feynman Prize in Nanotechnology

Schatz
2004 Elected to the National Academy of Sciences (Schatz)
2004 Named the Editor-in-Chief of the Journal of Physical Chemistry
2002 Morrison Professor of Chemistry, Northwestern University
2002 Elected to American Academy of Arts and Sciences
2001 Elected to International Academy of Quantum Molecular Science

Stupp
2005 American Chemical Society Award in Polymer Chemistry
2004 Visiting Professor, Institut de Science et d'Ingenierie Supramoleculaire, Université Louis Pasteur, Strasbourg, France
2004 Fellow, Biomaterials Science and Engineering, World Biomaterials Congress
2004 Merck-Karl Pfister Visiting Professorship in Organic Chemistry, Department of Chemistry, Massachusetts Institute of Technology
2003 Fellow, World Technology Network
2002 Chair Paris-Sciences, Ecole Supérieure de Physique et de Chimie Industrielles
2001 Chair, Review Committee of the National Nanotechnology Initiative, National Research Council